

Introduction

1.1 History of polymer science

Much of human history has been influenced by the availability of materials. In fact, history is divided into eras named after the primary materials used; the Stone Age, the Bronze Age, and the Iron Age. Similarly, we can assert that in the twentieth century we entered the Polymer Age.

Humans have used naturally occurring polymers, called biopolymers, for centuries without realizing that they were dealing with macromolecules. A prime example is caoutchouc, or natural rubber, that comes from *Hevea brasiliensis*, the rubber-tree plant. Natural rubber was used for many centuries before it was identified as polymeric.

Chemists started polymerizing synthetic macromolecules in the middle of the nineteenth century, but they did not believe that they were creating very large molecules. The standard point of view in the beginning of the twentieth century was that these materials were colloids—physically associated clusters of small molecules, with mysterious non-covalent bonds holding the clusters together. Many scientists actually measured high molar masses for these materials (of order 10^4 g mol^{-1} or even 10^5 g mol^{-1}), but rejected their own measurements because the values changed systematically with concentration. We now understand such changes with concentration, and the true molar mass, obtained by extrapolation to zero concentration, would have been even larger.

In 1920, Staudinger proposed the **macromolecular hypothesis**: polymers are molecules made of covalently bonded elementary units, called monomers. In this view, the colloidal properties of polymers were attributed entirely to the sizes of these large molecules, called **macromolecules** or **polymers**. In contrast to colloids, macromolecules exhibit colloidal properties in all solvents in which they dissolve, strongly suggesting that covalent bonds hold polymers together. Although this hypothesis initially met with strong resistance, its gradual acceptance during the 1920s allowed for substantial progress in the field in subsequent years. By 1929, Carothers had synthesized a variety of polymers with well-defined structures, and the Polymer Age was born.

During the following 30 years (1930–60), the main concepts of polymer science were established. Polymer synthesis tools were developed and refined during this period. Also, most of the foundations of polymer

Introduction

physics that are discussed in this textbook were introduced during this time period. These include the work of Kuhn on macromolecular sizes (Chapter 2), the work of Flory on swelling a single chain in a good solvent (Chapter 3), the work of Huggins and Flory on thermodynamics (Chapter 4), the work of Flory and Stockmayer on gelation (Chapter 6) and the work of Kuhn, James, and Guth on rubber elasticity (Chapter 7). The single-molecule models of polymer dynamics, were also developed during this period by Rouse and Zimm (Chapter 8).

In the subsequent 20 years (1960–80), the main principles of modern polymer physics were developed. These include the Edwards model of the polymer chain and its confining tube (Chapters 7 and 9), the modern view of semidilute solutions established by des Cloizeaux and de Gennes (Chapter 5), and the reptation theory of chain diffusion developed by de Gennes (Chapter 9) that led to the Doi–Edwards theory for the flow properties of polymer melts.

There are of course, many facets of polymers for which our understanding is far from complete. Polymers with associating groups bonded to their chains, polymer crystallization, liquid crystalline polymers and charged polymers are examples of areas of active research in polymer physics. These four particular examples are also very pertinent to understanding the functions of important biopolymers, such as DNA, RNA, proteins, and polysaccharides. By learning the fundamentals of chain conformations, thermodynamics, elasticity, and mobility, the readers of this book should be ready to consider these more challenging facets.

1.2 Polymer microstructure

The word (poly)-(mer) means (many)-(parts) and refers to molecules consisting of many elementary units, called **monomers**.¹ Monomers are structural repeating units of a polymer that are connected to each other by covalent bonds. Since ‘monomer’ can mean anything that repeats along the chain, it is by definition ambiguous. In this book, two types of monomers are important. Chemical monomers are the repeating unit that corresponds to the small molecules that were linked together to make the polymer chain. The repeating unit that will be most important for our discussions is a longer section of chain called the Kuhn monomer, that will be defined in Chapter 2. Here we focus on the chemical monomer.

The entire structure of a polymer is generated during **polymerization**, the process by which elementary units (chemical monomers) are covalently bonded together. The number of monomers in a polymer molecule is called its **degree of polymerization** N . The **molar mass** M of a polymer is equal to

¹ Chemists use the term ‘monomer’ to indicate an unreacted small molecule that is capable of polymerizing. Since this book is concerned with polymers, we often use ‘monomer’ to describe the repeating unit in a polymer chain, essentially a short form of ‘reacted monomer’.

its degree of polymerization N times the molar mass M_{mon} of its chemical monomer.²

$$M = NM_{\text{mon}}. \quad (1.1)$$

Consider, for example, the general structure of vinyl monomers and polymers shown in Fig. 1.1, where R represents different possible chemical moieties.

If the R group in Fig. 1.1 is hydrogen, the polymer is polyethylene. The repeating unit is $-\text{CH}_2-\text{CH}_2-$ and the polymer is called polyethylene because polymers are traditionally named after the monomers used in their synthesis (in this case ethylene, $\text{CH}_2=\text{CH}_2$), even though polymethylene with repeating unit $-\text{CH}_2-$ has an identical structure. To avoid potential complications arising from different monomers creating the same polymer, we often discuss the **number n of backbone bonds** instead of the degree of polymerization N , which is the number of monomers in the chain. If the R group in Fig. 1.1 is chlorine the polymer is poly(vinyl chloride), with repeating unit $-\text{CH}_2-\text{CHCl}-$, prepared from polymerization of vinyl chloride ($\text{CH}_2=\text{CHCl}$). If the R group in Fig. 1.1 is a benzene ring, the polymer is polystyrene.

The conventional way to describe the mass of a polymer chain is the **molar mass**: the mass of one mole (equal to **Avogadro's number** $\mathcal{N}_{\text{Av}} \cong 6.02 \times 10^{23} \text{ molecules mol}^{-1}$) of these molecules. For example, a polyethylene molecule consisting of $N = 1000$ chemical monomers, each with molar mass $M_{\text{mon}} = 28 \text{ g mol}^{-1}$, has a molar mass $M = 28\,000 \text{ g mol}^{-1}$. This means that \mathcal{N}_{Av} such molecules weigh 28 000 g or one molecule weighs

$$\begin{aligned} M/\mathcal{N}_{\text{Av}} &= 28\,000 \text{ g mol}^{-1} / (6.02 \times 10^{23} \text{ molecules mol}^{-1}) \\ &\cong 4.65 \times 10^{-20} \text{ g molecule}^{-1}. \end{aligned}$$

It is more convenient and therefore, customary to report the mass of such a polymer as $M = 28\,000 \text{ g mol}^{-1}$ rather than $4.65 \times 10^{-20} \text{ g molecule}^{-1}$. A related measure of the mass is the polymer **molecular weight**, with units of **Daltons (Da)** defined as 12 times the ratio of the polymer molar mass and the molar mass of ^{12}C . Hence, in the above example, the molecular weight is 28 000 Da.

The chemical identity of monomers is one of the main factors determining the properties of polymeric systems. Another major factor is the polymer's **microstructure**, which is the organization of atoms along the chain that is fixed during the polymerization process. In Fig. 1.1, once the double bond polymerizes, a variety of different isomers are possible for the repeating units along the chain. Polymer microstructure cannot be changed without breaking covalent chain bonds. Below we describe three

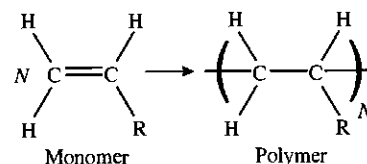


Fig. 1.1

Polymerization of vinyl monomers.

² End monomers typically have slightly different molar masses M'_{mon} and M''_{mon} . Therefore $M = M_{\text{mon}}(N - 2) + M'_{\text{mon}} + M''_{\text{mon}}$. However, the approximation $M \cong M_{\text{mon}}N$ is usually very good for large degrees of polymerization. For example, in polyethylene $M_{\text{mon}} = 28 \text{ g mol}^{-1}$, $M'_{\text{mon}} = M''_{\text{mon}} = 29 \text{ g mol}^{-1}$ and the error for $N = 100$ is 0.07%.

Fig. 1.2
The two sequence isomers of polypropylene.

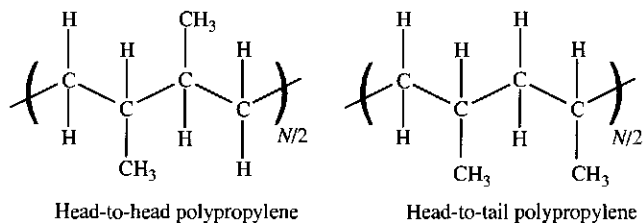
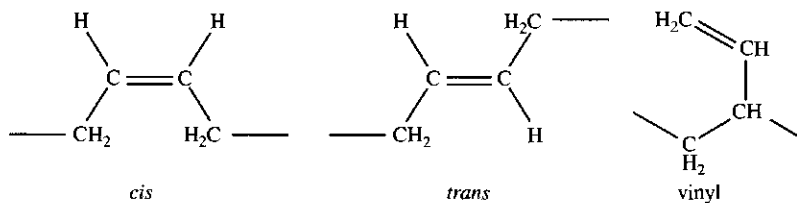


Fig. 1.3
The three structural isomers of polybutadiene.

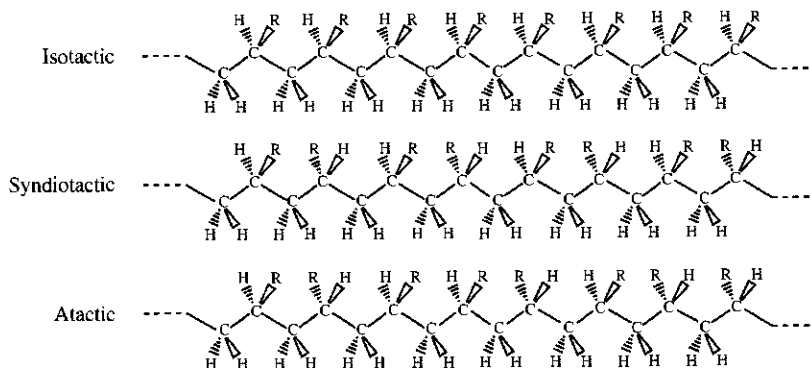


different categories of isomers: sequence, structural, and stereo isomerism. Examples of **sequence isomerism** are shown in Fig. 1.2 for polypropylene. In the **head-to-head isomer**, two adjacent monomers have their CH₃ groups attached to adjacent carbons along the chain's backbone, whereas the **head-to-tail isomer** has a CH₂ in the backbone between the CH₃ groups of adjacent monomers. Head-to-tail is the more common microstructure, but the properties change significantly with the fraction of head-to-head isomers present.

Polymers that contain a double bond in their backbone (that cannot rotate) can exhibit **structural isomerism**. Such polymers have distinct structural isomers, such as *cis*-, *trans*-, and vinyl-polybutadiene shown in Fig. 1.3. These isomers result from the different ways that dienes, such as butadiene, can polymerize and many synthetic polymers have mixtures of *cis* and *trans* structural isomers along their chains. A particular mixture reflects the probabilities of various ways that monomers add to the growing chain.

Another isomeric variation that is locked-in during polymerization of vinyl monomers is **stereoisomerism**. The four single bonds, emanating from a carbon atom, have a tetragonal structure. If all backbone carbon atoms of a polymer are arranged in a zig-zag conformation along the same plane, adjacent monomers can either have their R group on the same or different sides of this plane, as shown in Fig. 1.4. This type of stereoisomeric variation is described by the polymer's **tacticity**. If all of the R groups of a vinyl polymer are on the same side of the chain, the polymer is **isotactic**. On the other hand, if the R groups alternate regularly, the polymer is **syndiotactic**. Another possibility is that the placement of the R groups is completely random and such polymers are **atactic**. Vinyl polymers always have single C-C bonds along their backbone that allow rotations, but these rotations never change the locked-in nature of the polymer's tacticity. Many synthetic vinyl polymers do not correspond to one of the simple tacticities

Homopolymers and heteropolymers

**Fig. 1.4**

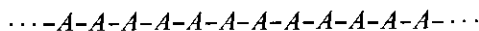
Tacticities of vinyl polymers, illustrated with all backbone carbons in the plane of the page and with H and R groups pointing either into or out from the page.

shown in Fig. 1.4. A more general case is described by a probability p_m for a monomer to add to the growing chain with its R group on the same side as the previous monomer (and probability $1 - p_m$ that the monomer adds with its R group on the opposite side). Often polymers have p_m near $1/2$, for example if R is Cl, commercial poly(vinyl chloride) has $p_m \cong 0.45$ and if R is benzene, commercial polystyrene has $p_m \cong 0.50$. Isotactic polymers correspond to $p_m = 1$, syndiotactic macromolecules have $p_m = 0$, and atactic ones have $p_m = 1/2$, but any probability $0 \leq p_m \leq 1$ is possible. Different polymerization schemes for a given monomer often result in a different p_m . Isomeric variations, such as sequence isomerism, structural isomerism and stereoisomerism are typically measured using NMR spectroscopy.

Physical properties of polymeric systems are strongly affected by chain microstructure. For example, it is much easier to crystallize isotactic and syndiotactic polymers than atactic ones.

1.3 Homopolymers and heteropolymers

Macromolecules that contain monomers of only one type are called **homopolymers**.



Homopolymers are made from the same monomer, but may differ by their microstructure, degree of polymerization or architecture. Examples of different microstructure of homopolymers such as tacticity, structural or sequence isomerisms were described in Section 1.2.

Throughout this book we demonstrate that the degree of polymerization N (or the number of backbone bonds n) of macromolecules is a major factor determining many properties of polymeric systems. If a molecule consists of only a small number of monomers (generally, less than 20) it is called an **oligomer**. Linear polymers contain between 20 and 10 billion (for the longest known chromosome) monomers. As monomers are linked together, the physical properties of molecules change. Both the boiling point and the melting point increase rapidly with the number of backbone

Table 1.1 Properties and applications of alkane hydrocarbons (following Sperling)

| Number of C atoms | State at 25°C | Example | Uses |
|-------------------|-----------------------|--------------|---------------------------|
| 1–4 | Simple gas | Propane | Gaseous fuels |
| 5–15 | Low-viscosity liquid | Gasoline | Liquid fuels and solvents |
| 16–25 | High-viscosity liquid | Motor oil | Oils and greases |
| 20–50 | Simple soft solid | Paraffin wax | Candles and coatings |
| >1000 | Tough plastic solid | Polyethylene | Bottles and toys |

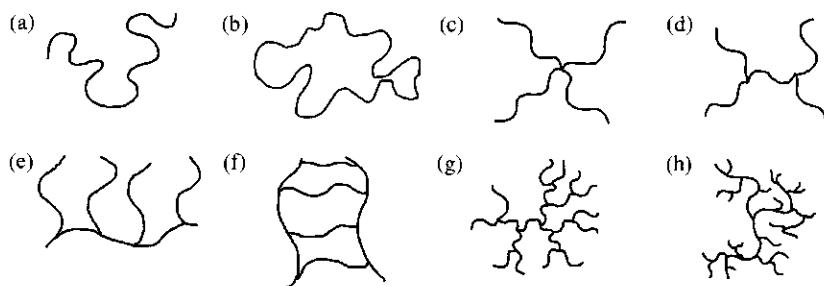


Fig. 1.5
Examples of polymer architectures:
(a) linear; (b) ring; (c) star; (d) H;
(e) comb; (f) ladder; (g) dendrimer;
(h) randomly branched.

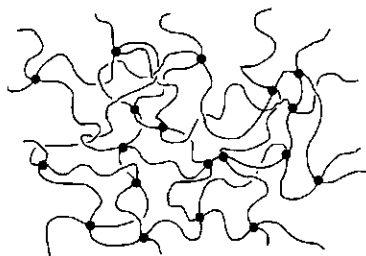


Fig. 1.6
Schematic architecture of a polymer network, with the dots indicating crosslinks.

bonds, resulting in different uses of these molecules, as shown in Table 1.1 for alkane hydrocarbons.

Another important feature controlling the properties of polymeric systems is polymer architecture. Types of polymer architectures include **linear**, **ring**, **star-branched**, **H-branched**, **comb**, **ladder**, **dendrimer**, or **randomly branched** as sketched in Fig. 1.5. Random branching that leads to structures like Fig. 1.5(h) has particular industrial importance, for example in bottles and film for packaging. A high degree of crosslinking can lead to a macroscopic molecule, called a **polymer network**, sketched in Fig. 1.6. Randomly branched polymers and the formation of network polymers will be discussed in Chapter 6. The properties of networks that make them useful as soft solids (erasers, tires) will be discussed in Chapter 7.

Combining several different types of monomers into a single chain leads to new macromolecules, called **heteropolymers**, with unique properties. The properties of heteropolymers depend both on composition (the fraction of each type of monomers present) and on the sequence in which these different monomers are combined into the chain. Macromolecules containing two different monomers are called **copolymers**. Copolymers can be **alternating**, **random**, **block**, or **graft** depending on the sequence in which their monomers are bonded together, as shown in Fig. 1.7. Polymers containing two blocks are called **diblock copolymers**. Chains with three blocks are called **triblock copolymers**. Polymers with many alternating blocks are called **multiblock copolymers** (Fig. 1.7).

Polymers containing three types of monomers are called **terpolymers** (Fig. 1.8). Examples of random terpolymers are **polyampholytes** containing positive, negative and neutral monomers. An example of block terpolymers are **ABC triblocks** shown in Fig. 1.8.

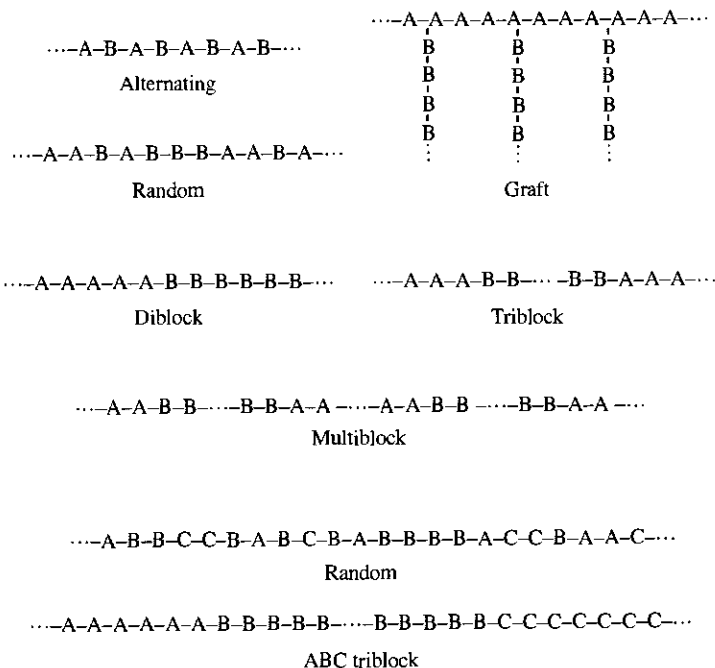


Fig. 1.7
Types of copolymers.

Fig. 1.8
Examples of terpolymers.

Many biopolymers are heteropolymers. DNA is a heteropolymer consisting of four different types of monomers (nucleotides), while natural **proteins** are heteropolymers commonly consisting of 20 different types of monomers (amino acids).

1.4 Fractal nature of polymer conformations

The polymer characteristics, described above—microstructure, architecture, degree of polymerization, chemical composition of heteropolymers—are all fixed during polymerization and cannot be changed without breaking covalent chemical bonds. However, after polymerization, a single flexible macromolecule can adopt many different **conformations**. A conformation is the spatial structure of a polymer determined by the relative locations of its monomers. Thus, a conformation can be specified by a set of n **bond vectors** between neighbouring backbone atoms. The conformation that a polymer adopts depends on three characteristics: flexibility of the chain, interactions between monomers on the chain, and interactions with surroundings. The inherent flexibility of the chain plays a vital role. Some chains are stiff like a piano wire, while others are quite flexible like a silk thread. There can be either attractive or repulsive interactions between monomers on the chain. The monomers also interact with their surroundings (either other chains or solvent) and the relative strengths of these various interactions can change with temperature. By tuning these effects, chain conformations change drastically, as will be explained in detail in Chapters 2–5.

To illustrate the magnitude of variations in chain dimensions, consider a chain of $n = 10^{10}$ bonds (one of the largest DNA molecules). The size of a bond is of the order of Angstroms and therefore, the contour length along the entire DNA molecule is of the order of meters. In order to get a better feeling for the range of scales involved, we magnify all lengths by the factor 10^8 to bring individual bond lengths onto a familiar size scale $l \approx 1$ cm. With strong attraction between monomers, the conformation of the polymer is a dense object, called a collapsed globule, occupying volume $V \approx nl^3 \approx 10^{10} \text{ cm}^3 \approx 10^4 \text{ m}^3$ and densely filling a large classroom of typical linear dimension $R \approx V^{1/3} \approx n^{1/3}l \approx 20$ m (see Fig. 1.9). If there are no interactions between monomers, in Chapter 2 it will be shown that the chain conformation is a random walk with size $R \approx n^{1/2}l \approx 1$ km, a typical campus dimension. Conformations of a polymer with excluded volume repulsions (to be described in detail in Chapter 3) are those of a self-avoiding walk with $R \approx n^{3/5}l \approx 10$ km, a typical city dimension. A polymer with long-range (such as electrostatic) repulsions adopts an extended conformation with size $R \approx nl \approx 10^5$ km, of the order of the distance to the

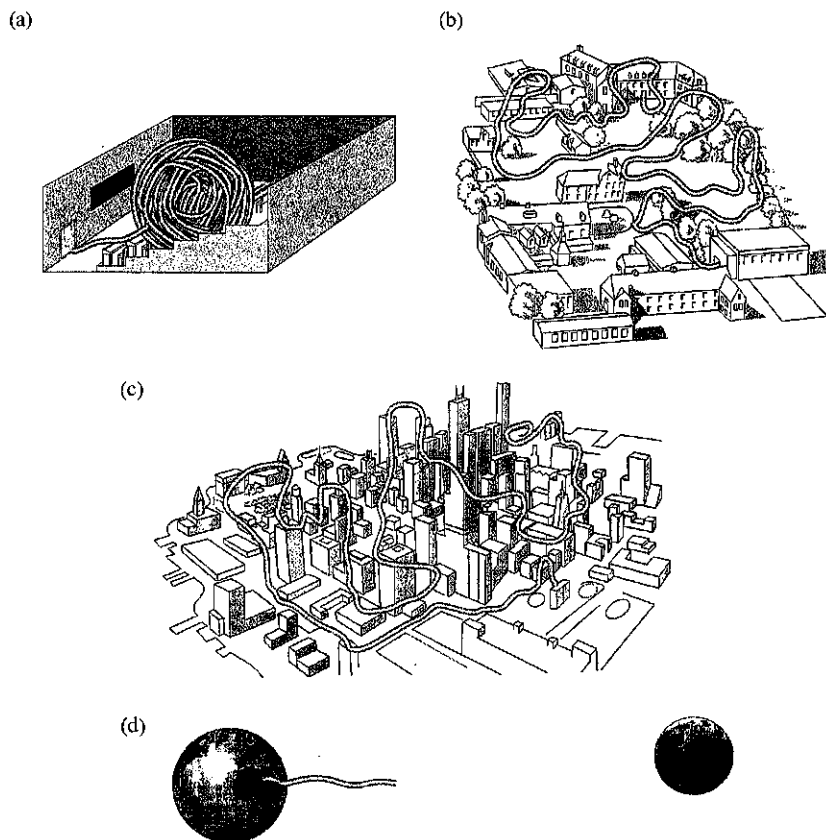


Fig. 1.9

A polymer's conformation is dictated by its interactions, here illustrated using a chain with 10^{10} monomers of size 1 cm and four types of interaction between monomers. (a) Attractive interaction—the chain fits in a classroom. (b) Zero effective interaction—the chain is the size of a campus. (c) Short-range repulsion—the chain is the size of a city. (d) Long-range repulsion—the size of a chain is a quarter of the distance to the Moon.

Moon! These astronomical variations of chain sizes make polymers a unique class of materials.

Another special feature of polymer conformations is that most of them are **self-similar (fractal)** over a wide range of length scales. In order to explain this important concept, we start with familiar objects, such as a solid ball of radius R . The volume V of this ball is approximately equal to the cube of its radius and proportional to its mass:

$$V = \frac{4\pi}{3} R^3 \cong 4.2R^3 \approx R^3 \sim \text{mass}. \quad (1.2)$$

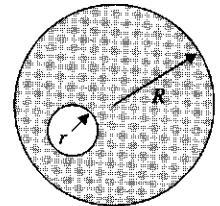
Throughout this book we will use the sign ' \cong ' to indicate a numerical approximation (i.e. $4\pi/3 \cong 4.2$) and the sign ' \approx ' to indicate that two quantities are proportional to each other up to a dimensionless prefactor of order unity ($4\pi/3$ in the example above). We will also use the notation ' \sim ' to indicate that the two quantities are proportional to each other up to a dimensional constant. The units of mass and volume are different. The meaning of proportionality ' \sim ' is that if the radius of the ball increases by a factor of 2, its mass increases by the factor $2^3 = 8$. The exponent in Eq. (1.2) is the dimension of the ball, $d=3$. Most of the objects we are familiar with are 3-dimensional. Relations similar to Eq. (1.2) are valid not only for the whole object, but for smaller parts of it as well. Indeed, consider cutting a small sphere of radius r out of this ball (Fig. 1.10). The mass m of this smaller ball is also proportional to the cube of its radius:

$$m \sim r^3. \quad (1.3)$$

Other dimensions we are familiar with are $d=2$ and $d=1$. An example of an almost two-dimensional object is a sheet of paper with uniform thickness and density (see Fig. 1.10). The mass m of the circle cut out of the piece of paper is proportional to the square of the radius r of this circle:

$$m \sim r^2. \quad (1.4)$$

Note that we have dropped all prefactors (both dimensionless and dimensional) in Eqs (1.3) and (1.4). A long wire is an example of an almost one-dimensional object (Fig. 1.11). The mass m of a piece of a wire is



Three-dimensional ball



Two-dimensional sheet of paper

Fig. 1.10
Examples of regular objects.

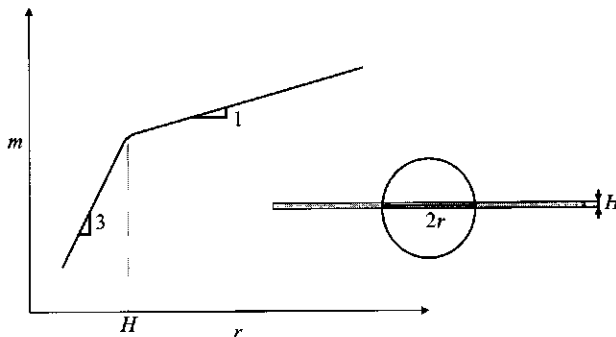


Fig. 1.11
Mass m of the part of the wire inside a sphere of radius r . Both axes have logarithmic scales.

proportional to the length $2r$ of this piece (if the diameter and density are uniform):

$$m \sim r. \quad (1.5)$$

In order to explain what we mean by the word ‘almost’, imagine a sphere of radius r around the wire. As long as the radius of the sphere r is much larger than the diameter H of the wire, the mass of material inside such an imaginary sphere would follow Eq. (1.5). But as soon as the radius of the sphere becomes smaller than the diameter H of the wire, its three-dimensional nature becomes important and the mass of the piece of wire inside the sphere changes proportionally to the cube of its radius [Eq. (1.3)]. The dependence of mass m of the part of the wire inside a sphere of radius r on the size of this sphere for a wire of diameter H is sketched in Fig. 1.11. Thus, we can say that the wire is one-dimensional on length scales much larger than its diameter $r \gg H$ and three-dimensional on smaller length scales $r \ll H$.

As the first example of a self-similar object, consider a regular fractal, called a triadic Koch curve (Fig. 1.12). We start from a section of straight line and divide it into three equal subsections (hence the name triadic) [Fig. 1.12(a)]. On the top of the middle subsection we draw an equilateral triangle and erase its bottom side (the original middle subsection of the line). Thus, we end up with four segments of equal length instead of the three original ones [Fig. 1.12(b)]. We repeat the above procedure for each of these four segments—divide each of them into three equal subsections and replace the middle subsections with the two opposite sides of equilateral triangles. At the end of the second step, we obtain a line with each of the four sections consisting of four smaller subsections [Fig. 1.12(c)]. This process can continue as long as your patience allows [Fig. 1.12(d) and (e)]. It is usually limited by the resolution of the computer screen or of the printer.

In order to calculate the dependence of the mass of the triadic Koch curve on the length scale, let us draw circles of diameter $2r$ equal to the lengths of the segments of two consecutive generations [Fig. 1.12(f)]. As we compare circles drawn around the segments of the consecutive generations of the curve, the radius of the circles changes by the factor of 3 ($r_1 = 3r_2$), while the mass m of the section of the curve inside these circles changes by the factor of 4 ($m_1 = 4m_2$). We are looking for an exponent \mathcal{D} defined by the relation

$$m \sim r^{\mathcal{D}}, \quad (1.6)$$

similar to Eqs (1.3)–(1.5) above. This exponent \mathcal{D} in Eq. (1.6) is called the **fractal dimension**. The fractal dimension for a triadic Koch curve can be determined from the fact that we have two ways to calculate m_1 in terms of r_2 ,

$$m_1 = Ar_1^{\mathcal{D}} = A(3r_2)^{\mathcal{D}}, \quad (1.7)$$

$$m_1 = 4m_2 = 4Ar_2^{\mathcal{D}}, \quad (1.8)$$

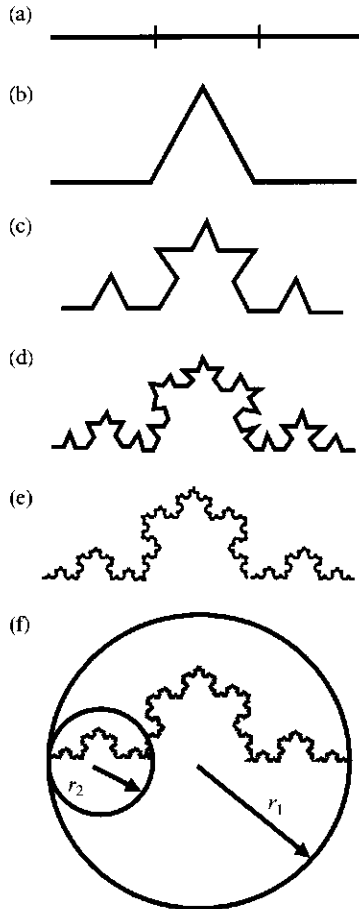


Fig. 1.12
Construction of a triadic Koch curve.

where A is the proportionality constant in Eq. (1.6). Equations (1.7) and (1.8) require

$$(3r_2)^D = 4r_2^D, \quad (1.9)$$

which can be solved for the fractal dimension of the triadic Koch curve.

$$D = \frac{\log 4}{\log 3} \cong 1.26. \quad (1.10)$$

Identical reasoning can be applied to any two consecutive generations of the Koch curve, making the exponent D [Eq. (1.10)] valid on all length scales. The self-similar nature of the Koch curve is clear from the fact that if a small piece of the curve is magnified, it looks exactly like the larger piece.

Another example of a regular fractal is a **Sierpinski gasket** shown in Fig. 1.13. Start with a filled equilateral triangle [Fig. 1.13(a)], draw the three medians that divide it into four smaller equilateral triangles and cut out the middle one [Fig. 1.13(b)]. In the second step, repeat the same procedure with each of the three remaining equilateral triangles, obtaining nine still smaller ones [Fig. 1.13(c)], and so on [Fig. 1.13(d) and (e)]. The fractal dimension of this Sierpinski gasket is calculated by the same method as for the Koch curve above [Fig. 1.13(f)]. As the radius of the circle around a section of the Sierpinski gasket doubles, the number of triangles (the mass of the gasket inside the circle) triples.

$$D = \frac{\log 3}{\log 2} \cong 1.58. \quad (1.11)$$

This approach can be applied to any fractal. If the size (the radius of a sphere) changes by the factor C_r ,

$$r_1 = C_r r_2, \quad (1.12)$$

while the mass inside this sphere changes by the factor C_m ,

$$m_1 = C_m m_2, \quad (1.13)$$

the fractal dimension is the ratio of the logarithms of these factors.

$$D = \frac{\log C_m}{\log C_r}. \quad (1.14)$$

There are many beautiful examples of regular fractals described and drawn in numerous books on this subject.

Polymers are random fractals, quite different from Koch curves and Sierpinski gaskets, which are examples of regular fractals. Consider, for example, a single conformation of an ideal chain, shown in Fig. 1.14. As will be discussed in detail in Chapter 2, the mean-square end-to-end distance of an ideal chain is proportional to its degree of polymerization.

$$N \sim \langle R^2 \rangle. \quad (1.15)$$

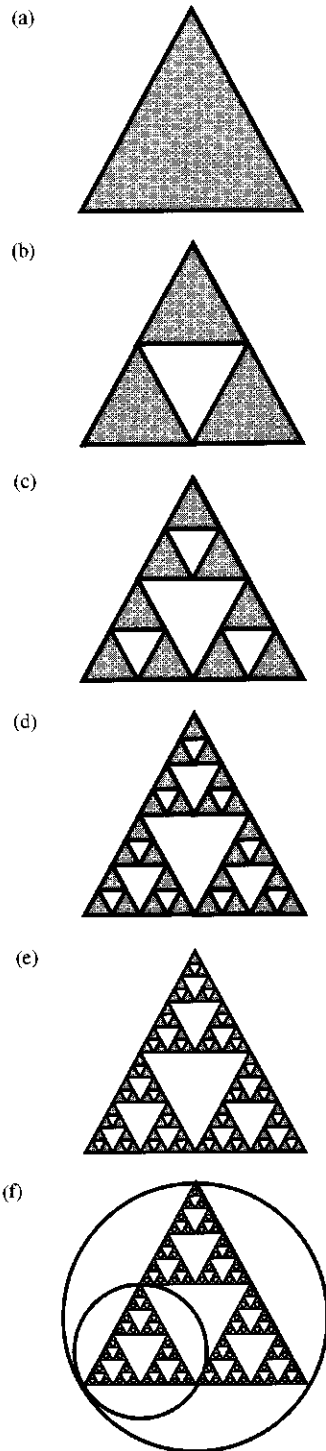


Fig. 1.13
Construction of a Sierpinski gasket.

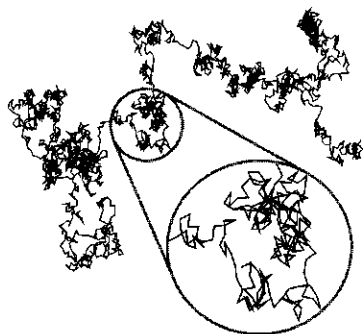


Fig. 1.14
Fractal structure of an ideal chain with fractal dimension $\mathcal{D} = 2$ obtained by computer simulation (courtesy of Q. Liao).

The brackets refer to averages over different possible conformations of the ideal chain. This relation should not be taken literally to be valid for each possible conformation, but rather on average for a distribution of conformations of a given type. A similar relation holds for any subsection of the ideal chain with g monomers and size r :

$$g \sim \langle r^2 \rangle. \quad (1.16)$$

Therefore, the fractal dimension of an ideal chain is $\mathcal{D} = 2$. The ideal chain is a self-similar object because if its smaller sections are magnified, they look like the whole chain (see Fig. 1.14). Unlike the regular fractals, such as the Koch curve, the magnified sections do not look exactly like the whole chain, but only on average (they have the same statistical properties, as will be explained in Chapter 2). Another distinction between regular fractals, such as the Sierpinski gasket, and polymeric fractals is that regular fractals are self-similar on *all* length scales. Polymeric fractals are self-similar on a finite, though possibly quite large, range of length scales. There is a natural cutoff of self-similarity on small length scales—the length l of the bond—and on large scales—the size R of the polymer. Thus, Eq. (1.16) is valid for $l < r < R$. The fractal dimension \mathcal{D} of any polymer is defined through the relation between the number of monomers g in any section of this polymer and the root-mean-square size $\sqrt{\langle r^2 \rangle}$ of this section:

$$g \sim \left(\sqrt{\langle r^2 \rangle} \right)^{\mathcal{D}}. \quad (1.17)$$

In Chapters 2, 3, 5, and 6, the fractal dimension \mathcal{D} of polymers will be derived in different conditions. Examples of the fractal dimensions of polymers are shown in Table 1.2.

Table 1.2 Fractal dimensions of polymers

| Architecture | Interactions | Space dimension d | \mathcal{D} |
|-------------------|------------------------------|---------------------|---------------|
| Linear | None | Any | 2 |
| Linear | Short-range repulsion | $d = 2$ | 4/3 |
| Linear | Short-range repulsion | $d = 3$ | 1.7 |
| Randomly branched | None | Any | 4 |
| Randomly branched | Short-range repulsion | $d = 2$ | 8/5 |
| Randomly branched | Short-range repulsion | $d = 3$ | 2.0 |
| Incipient gel | Partially screened repulsion | $d = 2$ | 91/48 |
| Incipient gel | Partially screened repulsion | $d = 3$ | 2.5 |

1.5 Types of polymeric substances

1.5.1 Polymer liquids

There are two types of **polymer liquids**: polymer melts and polymer solutions. **Polymer solutions** can be obtained by dissolving a polymer in a solvent. Examples of polymer solutions are wood protectants (varnish and

polyurethane coatings) and floor shines. Polymer solutions are classified as dilute or semidilute (Fig. 1.15) depending on the polymer **mass concentration** c , the ratio of the total mass of polymer dissolved in a solution and the volume of the solution. An alternative measure of concentration is the **volume fraction** ϕ , the ratio of occupied volume of the polymer in the solution and the volume of the solution. These two concentrations are related through the polymer density ρ :

$$\phi = \frac{c}{\rho} = c \frac{v_{\text{mon}} \mathcal{N}_{\text{Av}}}{M_{\text{mon}}}. \quad (1.18)$$

We used the fact that the polymer density is the ratio of monomer molar mass M_{mon} and monomer molar volume $v_{\text{mon}} \mathcal{N}_{\text{Av}}$ (v_{mon} is the occupied volume of a single chemical monomer).

$$\rho = \frac{M_{\text{mon}}}{v_{\text{mon}} \mathcal{N}_{\text{Av}}}. \quad (1.19)$$

A typical monomer volume is $v_{\text{mon}} \approx 100 \text{ \AA}^3$ and the corresponding monomer molar volume is $v_{\text{mon}} \mathcal{N}_{\text{Av}} \approx 60 \text{ cm}^3$.

The **pervaded volume** V is the volume of solution spanned by the polymer chain

$$V \approx R^3, \quad (1.20)$$

where R is the size of the chain. This volume is typically orders of magnitude larger than the occupied volume of the chain $v_{\text{mon}} \mathcal{N}$ (see Fig. 1.14). The fractal nature of polymers ($N \sim R^D$) with typical fractal dimension $D < 3$, means most of the pervaded volume is filled with solvent or other chains. The volume fraction of a single molecule inside its pervaded volume is called the **overlap volume fraction** ϕ^* or the corresponding **overlap concentration** c^* :

$$\phi^* = \frac{N v_{\text{mon}}}{V} \quad c^* = \frac{\rho N v_{\text{mon}}}{V}. \quad (1.21)$$

If the volume fraction ϕ of the polymer solution is equal to the overlap volume fraction ϕ^* , the pervaded volumes of macromolecules densely fill space and chains are just at overlap ($\phi = \phi^*$) (see Fig. 1.15).³

If the polymer volume fraction ϕ in solution is below the overlap volume fraction ϕ^* , the solution is called **dilute** ($\phi < \phi^*$). The average distance between chains in dilute solutions is larger than their size. Therefore, polymer coils in dilute solutions are far from each other swimming happily in surrounding solvent. Most properties of dilute solutions are very similar to pure solvent with slight modifications due to the presence of the polymer.

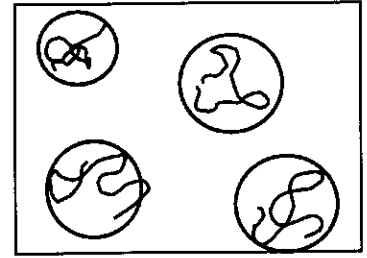
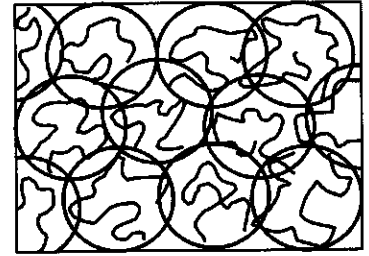
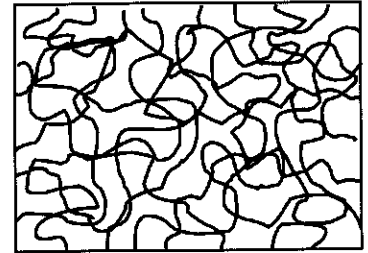
Dilute ($\phi < \phi^*$)Overlap ($\phi = \phi^*$)Semidilute ($\phi > \phi^*$)

Fig. 1.15
Solution regimes of flexible polymers.

³ In the definition of the overlap volume fraction ϕ^* , the pervaded volume V is taken at ϕ^* , since polymer size and hence its pervaded volume may change with concentration.

Solutions are called **semidilute** at polymer volume fractions above overlap (for $\phi > \phi^*$) (Fig. 1.15). This name comes from the fact that the actual values of volume fractions in these solutions are very low ($\phi \ll 1$). Most of the volume of a semidilute solution is occupied by the solvent. However, polymer coils overlap and dominate most of the physical properties of semidilute solutions (such as viscosity). Thus, adding a very small amount of polymer to a solvent can create a liquid with drastically different properties than the solvent. This unique feature of polymer overlap is due to their open conformations. Linear polymers in solution are fractals with fractal dimension $\mathcal{D} < 3$. In semidilute solutions, both solvent and other chains are found in the pervaded volume of a given coil. The **overlap parameter** P is the average number of chains in a pervaded volume that is randomly placed in the solution:

$$P = \frac{\phi V}{N V_{\text{mon}}}. \quad (1.22)$$

At the overlap volume fraction (for $\phi = \phi^*$) $P \equiv 1$, and as the concentration of linear chains is increased P steadily grows, reflecting the presence of additional chains inside the pervaded volume of each molecule. Notice that the overlap parameter counts the number of whole chains that share the pervaded volume. In reality, small parts of numerous chains are within each chain's pervaded volume in semidilute solution, and the overlap parameter counts these parts as though they were connected together into chains of N monomers. Use of Eq. (1.22) in semidilute solutions requires care because the chain size and hence, the pervaded volume V may change with concentration, as will be discussed in Chapter 5. The pervaded volume of a chain is not defined precisely, which makes ideas about overlap rather vague, meaning that both P and ϕ^* are somewhat imprecise. In practice this ambiguity is necessary because polymer overlap occurs over a range of concentrations.

In the absence of solvent, macromolecules can form a bulk liquid state, called a **polymer melt**. Polymer melts are neat polymeric liquids above their glass transition and melting temperatures. A macroscopic piece of a polymer melt remembers its shape and has elasticity on short time scales, but exhibits liquid flow (with a high viscosity) at long times. Such time-dependent mechanical properties are termed **viscoelastic** because of the combination of viscous flow at long times and elastic response at short times (viscoelasticity will be discussed in Chapters 8 and 9). A familiar example of a polymer melt is Silly Putty[®]. On short time scales (of order seconds), a sphere of Silly Putty resembles a soft elastic solid that bounces when dropped on the floor. However, if left on a table top for an hour, Silly Putty flows into a puddle like a liquid. In a polymer melt the overlap parameter is large ($P \gg 1$) and the strong overlap with neighbouring chains leads to entanglement that greatly slows the motion of polymers. However, individual chains in a polymer melt do move over large distances on long time scales, a property characteristic of fluids.

1.5.2 Polymer solids

There are several different types of polymeric solids. If a polymer melt is cooled, it can either transform into a **semicrystalline** solid below its **melting temperature** T_m or into a polymeric **glass** below its **glass transition temperature** T_g . Semicrystalline solids consist of crystalline regions, called **lamellae**, in which sections of chains are packed parallel to each other, and of amorphous regions between these lamellae (see Fig. 1.16). This multiphase nature makes semicrystalline polymers opaque, but also deformable and tough, when used at temperatures above the T_g of the amorphous phase (such as for polyethylene and polypropylene at room temperature). Macromolecules with regular configurations, such as isotactic and syndiotactic homopolymers often crystallize easily. Macromolecules with more random configurations, such as atactic homopolymers and random copolymers, tend to transform upon cooling into a transparent yet brittle glassy state (such as polymethylmethacrylate and polystyrene). However, there are technologically important exceptions to this rule. Polycarbonate, for example, is a tough glassy polymer at room temperature, making it the polymer of choice for transparent structural applications such as greenhouses and skylights.

If the chains of a polymer melt are reacted with each other to form covalent crosslinks between chains, a polymer network can be formed (Fig. 1.6). Polymer networks are solids and have a preferred shape determined during their preparation by crosslinking. Above their T_g , the chains between crosslinks in a polymer network can move locally, but not globally. Therefore, polymer networks above T_g are called soft solids. Rubbers or elastomers are crosslinked polymer networks with T_g below room temperature. Examples are vulcanized natural rubber (crosslinked polyisoprene) and silicone caulks (crosslinked polydimethylsiloxane). A **polymer gel** is a polymer network that is swollen in a solvent. The gel becomes progressively softer as more solvent is added, but always remains a solid owing to the permanent bonds that connect the chains. Examples of common polymer gels are Jello[®], which is a mixture of water and gelatin (a denatured form of the protein collagen collagen), and superabsorbers derived from poly(acrylic acid) used in disposable diapers.

1.5.3 Liquid crystal polymers

A variety of states with order intermediate between crystalline solids and amorphous liquids are also possible for polymers that contain sufficiently rigid rodlike monomers, known as **mesogens**. These mesogens can be attached to chemical monomers as a side group (the R group in Fig. 1.1) or they may be incorporated within the backbone of the polymer. Polymers with exclusively rigid rod-like mesogens as their monomers are usually intractable because they start to decompose below their crystalline melting points. However, alternating copolymers (Fig. 1.7) of rigid rodlike mesogens and flexible segments often are able to be melt processed and have interesting properties. In particular, in a temperature range between their

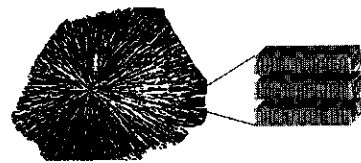


Fig. 1.16

Crystallization of polymer melts creates semicrystalline material consisting of folded chains in lamellae packed into a larger spherulitic structure, coexisting with amorphous regions.

melting point and the temperature at which they become isotropic liquids, these polymers can exhibit any of a number of phases with intermediate order.

A nematic phase, where the mesogens preferentially align in the same direction locally, is the least ordered and most common liquid crystalline phase. Often the alignment of the mesogens allows the molecules to slide past one another more easily, making the viscosity of the nematic phase lower than the isotropic liquid viscosity. A variety of smectic phases are also possible, where the mesogens form layered structures. These anisotropic liquid crystalline phases can occur in melts, solutions and networks. The physical properties of liquid crystal polymers are anisotropic as a result of the order. Additionally, electric fields, magnetic fields, and flow fields can be used to align this class of materials. It is important to realize that the polymer liquids and solids discussed in the remainder of this book are always assumed to be isotropic.

1.6 Molar mass distributions

One distinguishing feature of most synthetic polymers is that they are **polydisperse**. The entire polymer sample is made up of individual molecules that have a distribution of degrees of polymerization, determined by the particular synthesis method used. If all polymers in a given sample have the same number of monomers, the sample is **monodisperse**. There are many examples of natural polymers (such as proteins) that are perfectly monodisperse, but such perfection is very rare in synthetic polymers. The molar mass of a monodisperse polymer with degree of polymerization N is given by Eq. (1.1).

The polydispersity of a sample is described by its **molar mass distribution**. Polydisperse and monodisperse distributions are sketched in Fig. 1.17. A distribution is shown as n_N , the **number fraction** (or mole fraction) of molecules containing N monomers each, plotted as a function of molar mass $M_N = M_{\text{mon}}N$ of the molecules.

In practice, it is often more convenient to deal with the **weight fraction** w_N of molecules with molar mass M_N :

$$w_N = \frac{n_N M_N}{\sum_N n_N M_N} = \frac{n_N N}{\sum_N n_N N}. \quad (1.23)$$

The summation \sum_N is a shorthand notation for a sum over all possible values of N (i.e. $\sum_{N=1}^{\infty}$). The weight fraction w_N is related to the mass concentrations of various species (c_N is the mass of molecules with degree of polymerization N per unit volume)

$$w_N = \frac{c_N}{c}, \quad (1.24)$$

where c is the total mass concentration.

It is convenient to define the k th **moment** of the number fraction distribution as the sum of the products of the number fraction n_N of molecules

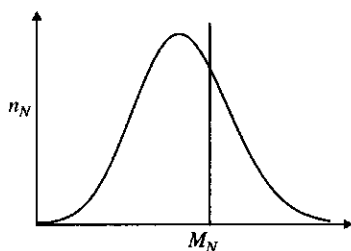


Fig. 1.17
Comparison of monodisperse and polydisperse molar mass distributions.

with degree of polymerization N and their molar mass raised to the k th power:

$$m_k = \sum_N n_N M_N^k. \quad (1.25)$$

The zeroth ($k=0$) moment is equal to unity because the number fraction distribution is normalized:

$$m_0 = \sum_N n_N = 1. \quad (1.26)$$

In order to characterize the molar mass distribution, several average molar masses are defined that emphasize different parts of this distribution. The **number-average molar mass** M_n is defined as the ratio of the first ($k=1$) to zeroth ($k=0$) moments of the number fraction distribution:

$$M_n \equiv \frac{m_1}{m_0} = \frac{\sum_N n_N M_N}{\sum_N n_N} = \sum_N n_N M_N. \quad (1.27)$$

The number-average is the common average used, for example, to determine the average denomination of the coins in your pocket. The number fraction of each type of coin (n_N) is multiplied by its denomination (M_N).

Substituting Eq. (1.27) into Eq. (1.23) shows that the ratio of the molar mass of a polymer with N monomers and the number-average molar mass M_n relates the number fraction and weight fraction of molecules:

$$w_N = \frac{M_N}{M_n} n_N = \frac{N}{N_n} n_N. \quad (1.28)$$

The final relation was obtained by introducing the number-average degree of polymerization $N_n \equiv M_n/M_{\text{mon}}$. The number-average is the quantity that is directly controlled by polymerization chemistry. The total number density of chains is the sum of the number density of all species:

$$\frac{cN_{\text{Av}}}{M_n} = \sum_N \frac{c_N N_{\text{Av}}}{M_N}. \quad (1.29)$$

Solving for M_n gives an alternative expression for calculating the number-average molar mass:

$$M_n = \frac{c}{\sum_N c_N/M_N} = \frac{1}{\sum_N w_N/M_N}. \quad (1.30)$$

The final relation was obtained using Eq. (1.24). For strictly linear polymers, each chain has exactly two ends, so the number-average molar mass can be measured by counting end groups using spectroscopy. However, many polymer properties are controlled by the longer chains in the molar mass distribution, making higher-order averages useful.

The **weight-average molar mass** M_w is the ratio of the second and the first moments of the number fraction distribution:

$$\begin{aligned} M_w &\equiv \frac{m_2}{m_1} = \frac{\sum_N n_N M_N^2}{\sum_N n_N M_N} = \frac{\sum_N n_N M_N^2}{M_n} = \sum_N w_N M_N \\ &= \sum_N \frac{c_N}{c} M_N. \end{aligned} \quad (1.31)$$

The last set of relations was obtained using the connection between weight and number fractions [Eqs (1.28) and (1.24)]. The weight-average is the molar mass obtained by randomly choosing the monomer. For example, consider a mixture of different length strings in a box. The weight-average length of the strings can be measured by reaching into the box (with eyes closed), pulling out one of the strings, measuring its length (with eyes open), putting it back into the box, mixing the strings and repeating the procedure many times. The probability of pulling a particular string out of the box is proportional to that string's length, since each section of string has the same probability of being selected.

In Section 1.7.2, we will see that the weight-average molar mass can be measured by light scattering from a dilute polymer solution. The viscosity of polymer liquids correlates well with the weight-average molar mass.

The **polydispersity index** is defined as the ratio of the weight-average and number-average molar masses M_w/M_n . Monodisperse samples with $M_w = M_n$ have polydispersity index $M_w/M_n = 1$. Larger polydispersity indices correspond to samples with broader molar mass distributions.

The **z-average molar mass** M_z is defined as the ratio of the third to the second moments of the number fraction distribution:

$$M_z \equiv \frac{m_3}{m_2} = \frac{\sum_N n_N M_N^3}{\sum_N n_N M_N^2} = \frac{\sum_N w_N M_N^2}{\sum_N w_N M_N} = \frac{\sum_N c_N M_N^2}{\sum_N c_N M_N}. \quad (1.32)$$

Similarly, the $(z+1)$ -average molar mass is the ratio of the fourth to the third moments of the number fraction distribution:

$$M_{z+1} \equiv \frac{m_4}{m_3} = \frac{\sum_N n_N M_N^4}{\sum_N n_N M_N^3} = \frac{\sum_N w_N M_N^3}{\sum_N w_N M_N^2} = \frac{\sum_N c_N M_N^3}{\sum_N c_N M_N^2}. \quad (1.33)$$

In general, the $(z+k)$ -average molar mass is defined as

$$M_{z+k} \equiv \frac{m_{k+3}}{m_{k+2}} = \frac{\sum_N n_N M_N^{k+3}}{\sum_N n_N M_N^{k+2}} = \frac{\sum_N w_N M_N^{k+2}}{\sum_N w_N M_N^{k+1}} = \frac{\sum_N c_N M_N^{k+2}}{\sum_N c_N M_N^{k+1}}. \quad (1.34)$$

Higher-order molar mass averages, such as M_z and M_{z+1} emphasize the high molar mass tail of the molar mass distribution. Molecular theories of polymer dynamics predict these higher-order averages are important, but

currently available characterization methods for measuring them have insufficient precision to be useful.

Political example. In order to better understand the difference between the number- and weight-averages, let us calculate the average population of a state in the USA. One possible way of obtaining an average is to ask each US senator for a population of their respective state (there are two senators from each of the 50 states) and average these 100 answers. The result would be the number-average population of a state. If, instead of getting answers from senators, who are too busy, we ask congressmen and average their answers, we would obtain the weight-average state population. The reason is that the number of congressmen from each state is proportional to the population of the corresponding state. In 2001, the number-average population of each state is 6×10^6 people per state and the weight-average state population is 12×10^6 people per state, making the polydispersity index 2.

1.6.1 Binary distributions

In this section, two examples of **binary mixtures** of two different monodisperse chain lengths are used to better understand the various molar mass averages.

Example 1

Consider a mixture containing number fraction $n_A = 1/2$ of the protein gelatin with molar mass $M_A = 10^5 \text{ g mol}^{-1}$ and number fraction $n_B = 1 - n_A = 1/2$ of gelatin dimers with molar mass $M_B = 2 \times 10^5 \text{ g mol}^{-1}$. What are the number- and weight-average molar masses of this sample and its polydispersity index?

The number-average molar mass of the sample is

$$M_n = m_1 = \sum_N n_N M_N = n_A M_A + n_B M_B = 1.5 \times 10^5 \text{ g mol}^{-1}. \quad (1.35)$$

The second moment of the distribution is calculated in a similar fashion:

$$m_2 = \sum_N n_N M_N^2 = n_A M_A^2 + n_B M_B^2 \quad (1.36)$$

The weight-average molar mass is the ratio of the second and first moments:

$$M_w = \frac{m_2}{m_1} = \frac{n_A M_A^2 + n_B M_B^2}{n_A M_A + n_B M_B} \cong 1.67 \times 10^5 \text{ g mol}^{-1}. \quad (1.37)$$

The polydispersity index of this binary mixture is the ratio of M_w and M_n :

$$\frac{M_w}{M_n} = \frac{n_A M_A^2 + n_B M_B^2}{[n_A M_A + n_B M_B]^2} = \frac{10}{9}. \quad (1.38)$$

Introduction

Notice that even though the chain lengths in the binary mixture differ by a factor of 2, the polydispersity index $M_w/M_n = 10/9 \cong 1.11$ is only slightly larger than its monodisperse value of $M_w/M_n = 1$.

Example 2

Consider an example similar to the one above, but with the binary mixture containing *weight* fraction $w_A = 1/2$ (rather than number fraction) of gelatin molecules with molar mass $M_A = 10^5 \text{ g mol}^{-1}$ and weight fraction $w_B = 1 - w_A = 1/2$ of gelatin dimers with molar mass $M_B = 2 \times 10^5 \text{ g mol}^{-1}$. What are the number- and weight-average molar masses of this sample and its polydispersity index?

Eqs (1.30) and (1.31) can be used to calculate number-average molar mass

$$M_n = \frac{1}{\sum_N w_N/M_N} = \frac{1}{(w_A/M_A) + (w_B/M_B)} \cong 1.33 \times 10^5 \text{ g mol}^{-1} \quad (1.39)$$

and weight-average molar mass

$$M_w = \sum_N w_N M_N = w_A M_A + w_B M_B = 1.5 \times 10^5 \text{ g mol}^{-1}. \quad (1.40)$$

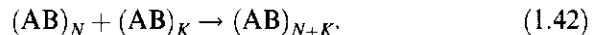
The polydispersity index of this binary mixture is the ratio of M_w and M_n :

$$\frac{M_w}{M_n} = [w_A M_A + w_B M_B] \left(\frac{w_A}{M_A} + \frac{w_B}{M_B} \right) = \frac{9}{8}. \quad (1.41)$$

This polydispersity index is larger than for the binary mixture in Example 1. Note that the arithmetic average of M_A and M_B ($1.5 \times 10^5 \text{ g mol}^{-1}$) is the number-average molar mass M_n for Example 1 with equal number fractions and is the weight-average molar mass M_w for Example 2 with equal weight fractions.

1.6.2 Linear condensation polymers

Consider linear condensation polymerization of monomers AB. An unreacted A group of any monomer is capable of forming a bond with any unreacted B group of any other monomer. Thus, an unreacted B group at the end monomer of an N -mer (molecule containing N monomers) can react with an unreacted A group at the end monomer of a K -mer, forming an $(N + K)$ -mer:



The ratio of the number of formed bonds to the maximum possible number of bonds in a reaction is called the **extent of reaction** p . If we select any group (A or B) randomly, p is the probability that the group has reacted. In linear condensation polymerization, each chain has one unreacted A group at one end of the chain and one unreacted B group at the other end. Flory

showed long ago that the reactivity of these groups is independent of chain length. Therefore, every A group of the original AB monomers has the same probability p to be reacted with some B group.

Next, we estimate the probability of a given A group to be at the end of an N -mer. To be at the end of the N -mer, this A group must be unreacted, with probability $1 - p$. The probability that the B group of this end monomer has reacted and formed a bond with the A group of the second monomer is p . There are $N - 1$ such polymerization bonds between monomers in any N -mer. The probability of forming these $N - 1$ independent bonds is p^{N-1} . The probability that the B group at the other end of the N -mer is unreacted is $1 - p$. Therefore, the probability that a given A group is at the end of an N -mer with $N - 1$ polymerization bonds and two unreacted groups at its ends is given by the product:

$$n(p, N) = p^{N-1}(1 - p)^2. \quad (1.43)$$

This probability is the number of N -mers *per monomer*: the number of N -mers in the sample at extent of reaction p divided by the total number of monomers in the system. The number of N -mers per monomer $n(p, N)$ is the ratio of the number density of N -mers $c_N \mathcal{N}_{Av} / (M_{\text{mon}} N)$ and the number density of all monomers $c \mathcal{N}_{Av} / M_{\text{mon}}$ in the sample

$$n(p, N) = \frac{c_N(p)}{cN} = \frac{w_N(p)}{N}, \quad (1.44)$$

where $c_N(p)$ is the mass concentration of N -mers at extent of reaction p and $w_N(p)$ is their weight fraction [Eq. (1.24)].

It is important to clarify the difference between the number of N -mers per monomer $n(p, N)$ and the number fraction $n_N(p)$ of N -mers (the number of N -mers per polymer chain) at extent of reaction p . The number fraction (or mole fraction) of N -mers was discussed in detail in the previous section. If we reach into the polymerization reactor at extent of reaction p and randomly select a *chain*, the probability that it has degree of polymerization N is the number fraction of N -mers:

$$n_N(p) = \frac{n(p, N)}{\sum_{N=1}^{\infty} n(p, N)} = N_n n(p, N) \quad (1.45)$$

The sum in the denominator is equal to the total number of molecules per monomer and hence, is the reciprocal of the number-average degree of polymerization $1/N_n$, thereby providing the final result in Eq. (1.45)

$$N_n = \frac{1}{\sum_{N=1}^{\infty} n(p, N)} = \frac{1}{(1 - p)^2 \sum_{N=1}^{\infty} p^{N-1}} = \frac{1}{(1 - p)^2 \sum_{k=0}^{\infty} p^k}. \quad (1.46)$$

The last equality was obtained by defining $k = N - 1$. The sum of the geometric series

$$\sum_{k=0}^{\infty} p^k = 1 + p + p^2 + p^3 + \dots \quad (1.47)$$

can be determined by multiplying it by p

$$p \sum_{k=0}^{\infty} p^k = p + p^2 + p^3 + \dots \quad (1.48)$$

leading to the equation

$$\sum_{k=0}^{\infty} p^k - p \sum_{k=0}^{\infty} p^k = 1 \quad (1.49)$$

with solution

$$\sum_{k=0}^{\infty} p^k = \frac{1}{1-p}. \quad (1.50)$$

Therefore, the number-average degree of polymerization has a simple form:

$$N_n = \frac{1}{\sum_{N=1}^{\infty} n(p, N)} = \frac{1}{1-p}. \quad (1.51)$$

Substituting this result into Eq. (1.45) we obtain the number fraction distribution for linear condensation polymers:

$$n_N(p) = \frac{n(p, N)}{\sum_{N=1}^{\infty} n(p, N)} = p^{N-1}(1-p). \quad (1.52)$$

This number fraction distribution [Eq. (1.52)] is shown as dashed line in Fig. 1.18 for the extent of reaction $p = 0.991$.

The weight fraction of N -mers is determined from Eqs (1.23) and (1.28):

$$w_N(p) = \frac{N}{N_n} n_N(p) = Np^{N-1}(1-p)^2. \quad (1.53)$$

If we reach into the polymerization reactor at extent of reaction p and randomly select a *monomer*, the weight fraction distribution $w_N(p)$ is the probability that the randomly chosen monomer is part of a chain with degree of polymerization N . Note that in general, the k -moment of the number fraction distribution is related to the $(k-1)$ -moment of the weight fraction distribution (see Problem 1.31):

$$\sum_N n_N M_N^k = M_n \sum_N w_N M_N^{k-1}. \quad (1.54)$$

Equations (1.52) and (1.53) are expressions of the number and weight fractions for the **most-probable distribution** of molecules expected for linear condensation polymerization. The most-probable weight fraction distribution $w_N(p)$ is compared with experimental data in Fig. 1.18. While the number fraction for the most-probable distribution is a monotonic function, the weight fraction has a maximum. The position of the maximum in

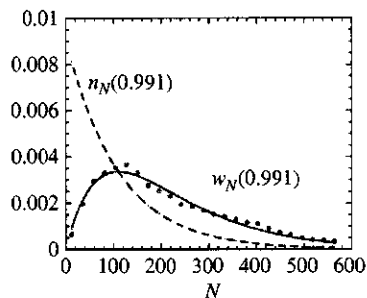


Fig. 1.18

Comparison of the most-probable weight fraction distribution $w_N(0.991)$ with experimental nylon 66 data from G. B. Taylor, *J. Am. Chem. Soc.* **69**, 638 (1947). The dashed line is the number fraction distribution $n_N(0.991)$.

the most-probable weight fraction distribution [Eq. (1.53) and the solid curve in Fig. 1.18]) is close to the number-average degree of polymerization

$$N_n = M_n/M_{\text{mon}} = 1/(1-p), \quad (1.55)$$

$N_n = 111$ for $p = 0.991$.

The number- and the weight-average molar masses are calculated from the moments of the molar mass distribution. The first moment of the number fraction distribution is the number-average molar mass M_n :

$$M_n = m_1 = M_{\text{mon}} \sum_{N=1}^{\infty} N n_N(p) = M_{\text{mon}}(1-p) \sum_{N=1}^{\infty} N p^{N-1}. \quad (1.56)$$

The summation can be carried out as follows:

$$\begin{aligned} \sum_{N=1}^{\infty} N p^{N-1} &= \frac{d}{dp} \sum_{N=1}^{\infty} p^N = \frac{d}{dp} \left[\sum_{N=0}^{\infty} p^N - 1 \right] \\ &= \frac{d}{dp} \left(\frac{1}{1-p} \right) = \frac{1}{(1-p)^2}. \end{aligned} \quad (1.57)$$

This leads to the number-average molar mass

$$M_n = m_1 = \frac{M_{\text{mon}}}{1-p}, \quad (1.58)$$

in agreement with the number-average degree of polymerization N_n [Eqs (1.51) and (1.55)]. The number-average molar mass M_n is larger than the monomer molar mass M_{mon} , and as p approaches unity (where all monomers are in a single chain) M_n gets extremely large (see Fig. 1.19).

The second moment of the number fraction distribution is obtained from Eq. (1.25) with $k=2$ and Eq. (1.52):

$$m_2 = M_{\text{mon}}^2 \sum_{N=1}^{\infty} N^2 n_N(p) = M_{\text{mon}}^2 (1-p) \sum_{N=1}^{\infty} N^2 p^{N-1}. \quad (1.59)$$

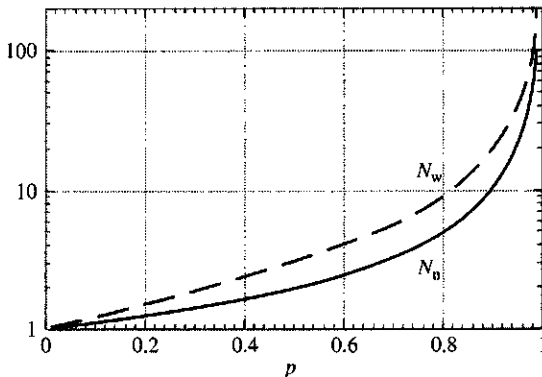


Fig. 1.19

Number-average (solid curve) and weight-average (dashed curve) degrees of polymerization as functions of extent of reaction for linear condensation polymerization.

The summation can be done by a procedure similar to Eq. (1.57):

$$\sum_{N=1}^{\infty} N^2 p^{N-1} = \frac{d}{dp} \left[p \frac{d}{dp} \sum_{N=0}^{\infty} p^N \right] = \frac{d}{dp} \left[\frac{p}{(1-p)^2} \right] = \frac{1+p}{(1-p)^3}. \quad (1.60)$$

Therefore, the second moment of the distribution is

$$m_2 = M_{\text{mon}}^2 \frac{1+p}{(1-p)^2}, \quad (1.61)$$

and the weight-average molar mass for linear condensation polymers is the ratio of Eqs (1.61) and (1.58):

$$M_w = \frac{m_2}{m_1} = M_{\text{mon}} \frac{1+p}{1-p}. \quad (1.62)$$

The weight-average molar mass for linear condensation polymers also diverges as the extent of reaction $p \rightarrow 1$ (see Fig. 1.19). The polydispersity index of the linear condensation polymers,

$$\frac{M_w}{M_n} = 1 + p, \quad (1.63)$$

approaches $M_w/M_n = 2$ for samples with high conversion ($p \rightarrow 1$) and high molar mass. Linear polymers prepared by condensation chemistry typically have $M_w/M_n \cong 2$ with a most-probable distribution of chain lengths.

The most-probable weight fraction distribution [Eq. (1.53)] can be approximated for large number-average degree of polymerization N_n by an exponential representation, utilizing the expansion of the logarithm for p near unity $\ln p \cong p - 1$ and Eq. (1.55) for N_n :

$$p^N = \exp(N \ln p) \cong \exp(-N(1-p)) = \exp\left(-\frac{N}{N_n}\right). \quad (1.64)$$

Thus, the most-probable weight fraction distribution can be approximated by a linear function with an exponential cutoff

$$w_N(p) = Np^{N-1}(1-p)^2 \cong \frac{N}{N_n^2} \exp\left(-\frac{N}{N_n}\right), \quad (1.65)$$

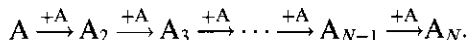
for large extents of reaction $p \rightarrow 1$ ($N_n \gg 1$). The most-probable number fraction distribution [Eq. (1.52)] for linear condensation polymers can also be approximated by an exponential form for large N_n :

$$n_N(p) = \frac{N_n}{N} w_N(p) \cong \frac{1}{N_n} \exp\left(-\frac{N}{N_n}\right). \quad (1.66)$$

This is the first of many examples where the molar mass distributions are products of simple functions and exponential cutoffs.

1.6.3 Linear addition polymers

In addition polymerization, monomers are added one at a time to a growing chain by propagation of a free radical through a liquid of monomers:



In the case of addition polymerization without termination, the number fraction distribution function (the probability that a given chain has degree of polymerization N) is given by the **Poisson distribution** function:

$$n_N = \frac{(N_n - 1)^{N-1}}{(N-1)!} \exp(1 - N_n). \quad (1.67)$$

The weight fraction distribution function for addition polymerization without termination is determined using Eq. (1.28):

$$w_N = \frac{N}{N_n} n_N = \frac{N(N_n - 1)^{N-1}}{N_n(N-1)!} \exp(1 - N_n). \quad (1.68)$$

The polydispersity index for the Poisson distribution is quite narrow, since there is no termination (see Problem 1.37):

$$\frac{N_w}{N_n} = 1 + \frac{1}{N_n} - \frac{1}{N_n^2} \quad (1.69)$$

Many addition polymerization reactions with very low concentrations of impurities have propagation rates much faster than initiation rates and have essentially no termination. Such reactions produce narrow molar mass distributions that can be approximated by the Poisson distribution. Comparison of the polydispersity index of anionically polymerized butadiene with Eq. (1.69) is shown in Fig. 1.20.

The experimental data lie above the prediction of Eq. (1.69) because the experimental determination of polydispersity index by size exclusion chromatography (Section 1.7.4) systematically overestimates M_w/M_n . The low molar mass polydispersity index does follow the trend expected by Eq. (1.69). The prediction of Eq. (1.69) that $M_w/M_n \cong 1$ for chains with $N_n \geq 1000$ (or $M_n \geq 10^5$) is never realized in practice because real polymerization reactions always have some impurities present.

Many addition polymerizations that involve free radicals at chain ends have termination reactions when two growing chain ends meet, and more generally termination can occur when a growing chain end meets an impurity. For addition polymerization with termination the **Shultz distribution** is used,

$$w_N = \frac{1}{N_n \Gamma(s)} \left(\frac{sN}{N_n} \right)^s \exp\left(-\frac{sN}{N_n}\right), \quad (1.70)$$

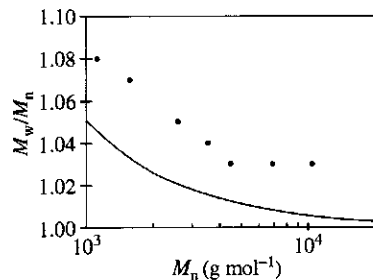


Fig. 1.20

Polydispersity index for polybutadienes polymerized using *s*-butyl lithium initiator in cyclohexane. The curve is the Poisson distribution prediction [Eq. (1.69)]. The ordinate data appear discretized because M_w/M_n can only be determined to three significant figures.

where $\Gamma(s)$ is the Gamma function.⁴ Note that for $s = 1$ the most-probable distribution is recovered [compare with Eq. (1.65)]. The polydispersity index of the Shultz distribution [Eq. (1.70)] is

$$\frac{N_w}{N_n} = \frac{s+1}{s}, \quad (1.71)$$

which leads to $N_w/N_n = 2$ for the most-probable distribution, but allows for broader ($N_w/N_n > 2$ for $s < 1$) and narrower ($1 < N_w/N_n < 2$ for $s > 1$) distributions.

1.7 Molar mass measurements

There are a variety of experimental methods available for determining different average molar masses and molar mass distributions. These methods utilize dilute solutions, and often require measurements at several concentrations so that an extrapolation to the limit of zero concentration can be made. Different methods are applicable to different ranges of polymer molar masses. Table 1.3 summarizes common characterization methods. Here we discuss only the four most common methods in detail.

Table 1.3 Molar mass measurement methods

| Method | Absolute | Relative | M_n | M_w | A_2 | Range (g mol ⁻¹) |
|---|----------|----------|-------|-------|-------|------------------------------|
| End group analysis | × | | × | | | $M_n < 10\,000$ |
| Vapor pressure osmometry | × | | × | | × | $M_n < 30\,000$ |
| Cryoscopy | × | | × | | × | $M_n < 30\,000$ |
| Ebulliometry | × | | × | | × | $M_n < 30\,000$ |
| Membrane osmometry | × | | × | | × | $20\,000 < M_n$ |
| Light scattering (LS) | × | | | × | × | $10^4 < M_w < 10^7$ |
| Intrinsic viscosity (IV) | | × | | | | $M < 10^6$ |
| SEC ^a with <i>c</i> detector | | × | × | × | | $10^3 < M < 10^7$ |
| SEC ^a with <i>c</i> and LS detectors | × | | | × | | $10^4 < M < 10^7$ |
| SEC ^a with <i>c</i> and IV detectors | | × | × | × | | $10^3 < M < 10^6$ |
| MALDI-TOF-MS ^b | × | | × | × | | $M < 10\,000$ |

^aSEC, size exclusion chromatography. ^bMALDI-TOF-MS, matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy.

1.7.1 Measuring M_n by osmotic pressure

Number-average molar mass can be determined directly by end group analysis, typically using infrared or nuclear magnetic resonance spectroscopies. Colligative solution properties (sensitive to the number of polymers

⁴ The Gamma function is defined as $\Gamma(a) = \int_0^\infty e^{-x} x^{a-1} dx$. Gamma functions of different arguments are related by $\Gamma(a+1) = a\Gamma(a)$. For integer values of a , the Gamma function is simply a factorial $\Gamma(a+1) = a!$.

present) also determine M_n from dilute solutions of the polymer. These include osmotic pressure, lowering of solvent vapor pressure, ebulliometry (elevation of boiling point), or cryoscopy (depression of freezing point). The most common method to measure M_n is osmotic pressure.

Osmotic pressure is a thermodynamic colligative property that measures the free energy difference between a polymer solution and a pure solvent [see Eq. (4.62) for the proper definition of osmotic pressure]. In practice, the two are separated by a membrane that allows solvent to pass through easily, but restricts polymer to stay on one side, as shown schematically in Fig. 1.21.

There is a free energy gain in mixing polymer with solvent (discussed in detail in Chapter 4) that makes more solvent flow into the solution with the polymer. This solvent flow continues until a pressure difference across the membrane balances the chemical potential of solvent on the two sides of the membrane. This pressure difference is the osmotic pressure, Π . In the limit of very dilute solutions, individual polymer coils do not interact with each other, and the osmotic pressure in sufficiently dilute solutions is equivalent to the pressure of an ideal gas. Polymer molecules cannot pass through the membrane and impose pressure on it similar to the pressure on the walls of the container by the molecules of an ideal gas. In both cases the pressure is equal to the **thermal energy** kT ($k = 1.38 \times 10^{-23} \text{ J K}^{-1}$ is the Boltzmann constant and T is absolute temperature) times the number density of molecules. For a monodisperse polymeric sample, the number density of chains is cN_{Av}/M , leading to the **van't Hoff Law**:

$$\lim_{c \rightarrow 0} \frac{\Pi}{c} = kT \frac{N_{\text{Av}}}{M} = \frac{\mathcal{R}T}{M}, \quad (1.72)$$

$\mathcal{R} = kN_{\text{Av}} \cong 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the gas constant. Since osmotic pressure is a colligative property, it is simply proportional to the number density of solute molecules that cannot cross the membrane, regardless of the length of the chains. For a polydisperse sample, the contribution to the osmotic pressure from polymers with different molar masses M_i and concentrations c_i are simply added:

$$\lim_{c \rightarrow 0} \frac{\Pi}{c} = \frac{\mathcal{R}T}{c} \sum_i \frac{c_i}{M_i} = \frac{\mathcal{R}T}{M_n}. \quad (1.73)$$

The final relation was obtained using Eq. (1.30). Hence, *dilute osmotic pressure measurements give the number-average molar mass of a polydisperse polymer sample*.

In order to obtain the number-average molar mass of a particular sample, **osmotic coefficient** (Π/c) data, measured at various low concentrations, must be extrapolated to the zero concentration limit. In addition to the ideal gas contribution [Eq. (1.73)] that arises from individual polymers, the osmotic pressure also has a contribution from polymer–polymer interactions. The contribution to osmotic pressure from interaction

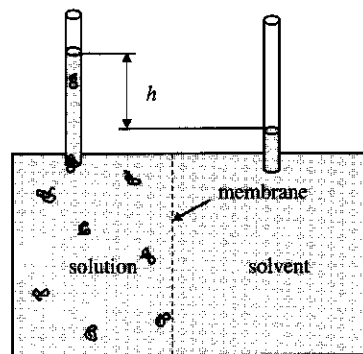


Fig. 1.21

Schematic representation of a membrane osmometer. The osmotic pressure is determined from the height difference h as $\Pi = \rho gh$, where ρ is the solvent density and g is the gravitational acceleration.

between species i and j is represented by $A_{ij}c_i c_j \mathcal{R}T$, where A_{ij} is called the **second virial coefficient** between species i and j . The total contribution from pairwise interactions to the osmotic pressure is the sum over all pairs of species i and j :

$$\begin{aligned}\Pi &= \mathcal{R}T \left(\frac{c}{M_n} + \sum_i \sum_j A_{ij} c_i c_j + \dots \right) \\ &= \mathcal{R}T \left(\frac{c}{M_n} + A_{2,w} c^2 + \dots \right).\end{aligned}\quad (1.74)$$

The coefficient $A_{2,w}$ in front of the c^2 term is the weight-average second virial coefficient (to be discussed in Chapter 3):

$$A_{2,w} \equiv \frac{1}{c^2} \sum_i \sum_j A_{ij} c_i c_j = \sum_i \sum_j A_{ij} w_i w_j, \quad (1.75)$$

where w_i is a weight fraction of species i ($w_i = c_i/c$). The subscript w is often dropped and the second virial coefficient is usually denoted by A_2 . The sign of the second virial coefficient A_2 indicates repulsion or attraction between chains. Positive values of A_2 result in increased osmotic pressure and correspond to repulsion between polymers. Conversely, negative values ($A_2 < 0$) correspond to attraction between chains. Strong attraction between chains may lead to phase separation. Molar masses of polymers *cannot* be obtained from osmotic pressure measurements in a phase separated sample.

By plotting $\Pi/c\mathcal{R}T$ against concentration (Fig. 1.22) the number-average molar mass is determined as the reciprocal of the intercept and the weight-average second virial coefficient is the slope:

$$\frac{\Pi}{c\mathcal{R}T} = \frac{1}{M_n} + A_{2,w}c + \dots \quad (1.76)$$

At higher concentrations, the higher-order virial terms have to be taken into account and extrapolation to zero concentration becomes more difficult.

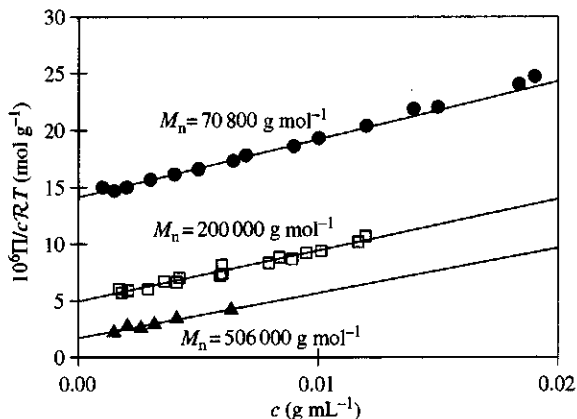


Fig. 1.22 Concentration dependence of osmotic coefficient for three poly(α -methylstyrene) samples in toluene at 25°C. The data corresponding to dilute solutions for these three samples are shown, with lines fit to the lowest concentration data. Data over wider ranges of concentration and chain length are shown in Fig. 5.7 [data from I. Noda, N. Kato, T. Kitano and M. Nagasawa, *Macromolecules* **16**, 668 (1981)].

1.7.2 Measuring M_w by scattering

Weight-average molar mass can be measured by scattering and by ultracentrifugation. Recent developments in photodetector technology have allowed light scattering to completely displace the ultracentrifuge as the method of choice for determining M_w . This section will focus on the scattering of visible light, although the same basic principles apply to scattering of other forms of radiation. Other forms of radiation used for studying polymers include X-rays (where the **scattering contrast** arises from electron density differences) and neutrons (where the scattering contrast comes from differences in atomic nuclei). Light scattering, on the other hand, relies on differences in refractive index n for scattering contrast (polarization of electron clouds). To measure the molar mass of a polymer chain, a dilute solution is prepared in a solvent with sufficiently different refractive index than the polymer. Usually a solvent can be found with refractive index differing from the polymer by $\Delta n \gtrsim 0.1$, making the **refractive index increment** $dn/dc \gtrsim 0.1 \text{ ml g}^{-1}$.

1.7.2.1 Scattering from gases

In order to understand the principle of **light scattering**, consider a gas of N_{tot} relatively small (compared to the wavelength of light λ) non-interacting molecules in a **scattering volume** V . The scattering volume is the portion of the sample that is illuminated by the incident beam and seen by the detector. In the simplest scattering geometry, the light source, the sample and the detector are all aligned in the horizontal yz plane (Fig. 1.23). An incident wave (a vertically polarized laser beam) travels from left to right along the z -axis. Light scattered by an angle θ in the horizontal yz plane is analysed by a detector.

The incident light produces oscillating electric and magnetic fields in the transverse direction (in the xy plane) at every point along the beam. In a typical case of a vertically polarized laser light, the electric field oscillates

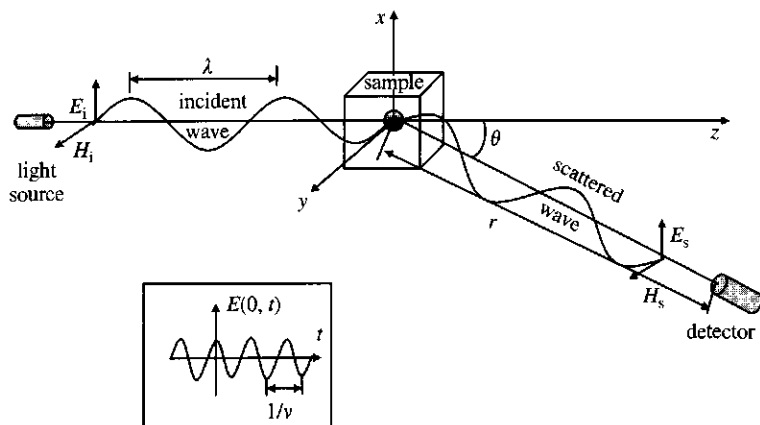


Fig. 1.23

Schematic geometry of Rayleigh scattering. Insert: oscillations in time of the electric field, $E(0, t)$, felt by a molecule at the origin.

along the vertical x axis, while the magnetic field oscillates along the y axis. The electric field at location z at time t along the wave is sinusoidal:

$$E(z, t) = E_i \cos \left[2\pi \left(\nu t - \frac{z}{\lambda} \right) \right]. \quad (1.77)$$

The oscillations of this electric field have amplitude E_i and frequency ν . The wavelength λ is the period of the wave in space. It is related to the period of oscillations in time $1/\nu$ through the speed of light $c \cong 2.998 \times 10^8 \text{ ms}^{-1}$:

$$\nu = \frac{c}{\lambda}. \quad (1.78)$$

The same relation is valid in a dielectric medium, such as a polymer solution, where both the speed c/n and the wavelength λ/n of light are reduced by the refractive index n of the medium.

Consider a molecule, located at the origin. It experiences time oscillations of the electric field from the beam (see insert in Fig. 1.23)

$$E(0, t) = E_i \cos \left(2\pi \frac{c}{\lambda} t \right). \quad (1.79)$$

This field causes the electrons in the molecule to oscillate, resulting in an induced dipole moment p proportional to the applied field:⁵

$$p = \alpha E = \alpha E_i \cos \left(2\pi \frac{c}{\lambda} t \right). \quad (1.80)$$

Here α is the **polarizability** of the molecule. An oscillating dipole emits electromagnetic waves in *all directions* with electric field proportional to the acceleration of charges (d^2p/dt^2) and decaying reciprocally with the distance r from the molecule. For a detector located in the horizontal yz plane at distance $r = \sqrt{y^2 + z^2}$ from the origin (see Fig. 1.23) the scattered wave has electric field

$$E_s = \frac{1}{c^2} \frac{1}{r} \left. \frac{d^2p}{dt^2} \right|_{t=t-r/c} = -\frac{4\pi^2}{\lambda^2 r} \alpha E_i \cos \left[2\pi \frac{c}{\lambda} \left(t - \frac{r}{c} \right) \right], \quad (1.81)$$

where the delay r/c is the time it takes the wave to travel from the oscillating dipole at the origin to the detector.

The **intensity** I_s of the wave scattered by a single molecule is proportional to the mean-square average of the field and is therefore related to the intensity I_i of the incident wave:

$$I_s = \frac{16\pi^4}{\lambda^4 r^2} \alpha^2 I_i. \quad (1.82)$$

The inverse fourth power dependence of the scattered intensity I_s on the wavelength λ was first understood by Lord Rayleigh. It explains the blue color of the sky since molecules in the Earth's atmosphere scatter the solar

⁵ Our discussion of electromagnetic radiation uses the cgs system of units.

light of shorter wavelengths (blue) with greater intensity than the longer wavelengths.

The intensity of light scattered by all $N_{\text{tot}}/V = cN_{\text{Av}}/M$ molecules in a unit volume is the sum of intensities from each individual molecule,

$$\bar{I} = \frac{cN_{\text{Av}}}{M} \frac{16\pi^4}{\lambda^4 r^2} \alpha^2 I_i, \quad (1.83)$$

where c is the mass concentration and M is the molar mass of the molecules. This simple addition of intensities is valid because there is no coherence between light scattered by non-interacting molecules. If we also assume that the distance r from all scattering particles to the detector is approximately the same, then the measured intensity is the product of the scattering volume V and the intensity scattered per unit scattering volume \bar{I} . In practice, this assumption is improved by moving the detector further from the sample or by making the scattering volume smaller, but either choice decreases the scattered intensity.

1.7.2.2 Scattering from dilute polymer solutions

The above results can be generalized to scattering from solutions, as long as there is contrast (difference in refractive indices) between solute and solvent. However, polymers can only be treated as point source scatterers in the limit of small scattering angles.⁶ Adding molecules with small number density $cN_{\text{Av}}/M \ll 1/\alpha$ to a solvent with refractive index n_0 leads to a linear change in dielectric constant, and hence a linear change in the square of the refractive index n of the solution:⁷

$$n^2 = n_0^2 + 4\pi\alpha \frac{cN_{\text{Av}}}{M}. \quad (1.84)$$

Differentiating both sides of Eq. (1.84) with respect to concentration c , provides the expression for the molecular polarizability (with units of volume):

$$\alpha = \frac{n}{2\pi} \frac{dn}{dc} \frac{M}{N_{\text{Av}}}. \quad (1.85)$$

Substituting this expression for the molecular polarizability α into Eq. (1.83) gives the intensity per unit scattering volume of vertically polarized light scattered in the horizontal plane:

$$\bar{I} = \frac{4\pi^2 n^2}{\lambda^4 r^2} \left(\frac{dn}{dc} \right)^2 \frac{cM}{N_{\text{Av}}} I_i. \quad (1.86)$$

The scattered intensity per unit scattering volume \bar{I} normalized by the incident intensity I_i and corrected for the $1/r^2$ distance dependence is called the **Rayleigh ratio**.⁸

$$R_\theta \equiv \frac{\bar{I} r^2}{I_i} \quad (1.87)$$

⁶ Precisely how small the scattering angle must be is discussed in Section 2.8.

⁷ The square of the refractive index is the dielectric constant of the medium.

⁸ The pure solvent always has some small scattering intensity due to density fluctuations. In practice, this solvent background scattering is subtracted from the Rayleigh ratio.

The unit of the Rayleigh ratio is inverse length (m^{-1}) since I_i is the incident intensity and \bar{I} is the scattered intensity per unit volume. The Rayleigh ratio describes the attenuation of the incident beam upon passing through a medium. The Rayleigh ratio for vertically polarized light scattered in the horizontal plane is

$$R_\theta = \frac{\bar{I}^2}{I_i} = \frac{4\pi^2 n^2}{\lambda^4} \left(\frac{dn}{dc} \right)^2 \frac{cM}{\mathcal{N}_{Av}} = KcM, \quad (1.88)$$

where we have defined an **optical constant**

$$K = \frac{4\pi^2 n^2}{\lambda^4 \mathcal{N}_{Av}} \left(\frac{dn}{dc} \right)^2. \quad (1.89)$$

Expression (1.88) is valid for very low concentrations ($c < c^*$) or for non-interacting molecules. In a polydisperse solution, each species j with molar mass M_j contributes $Kc_j M_j$ to the Rayleigh ratio. Therefore, the total Rayleigh ratio for a polydisperse system is given by the sum

$$R_\theta = K \sum_j c_j M_j = K c M_w. \quad (1.90)$$

The final relation was obtained using Eq. (1.31). Hence, *dilute scattering measurements give the weight-average molar mass of a polydisperse polymer sample.*

At low concentrations, polymer interactions make a contribution to the scattering proportional to the second virial coefficient, just as in the case of osmotic pressure [see Eq. (1.74)]. The contrast required for scattering from polymer solutions primarily comes from concentration fluctuations, which are controlled by the rate of change of osmotic pressure with concentration. For wavelengths much larger than the molecules, the scattering intensity is related to the **osmotic compressibility** ($c\partial\Pi/\partial c$).

$$\frac{Kc}{R_\theta} = \frac{1}{\mathcal{R}T} \left(\frac{\partial\Pi}{\partial c} \right)_T = \frac{1}{M} + 2A_2c + \dots, \quad (1.91)$$

The Rayleigh ratio for monodisperse samples can then be rewritten as:

$$R_\theta = \frac{KcM}{1 + 2A_2cM + \dots}. \quad (1.92)$$

In a polydisperse sample there are contributions to scattering from all species, which can be rewritten using the fact that $1/(1+x) \cong 1-x$ for small x :

$$\begin{aligned} R_\theta &= K \sum_i \frac{c_i M_i}{1 + 2 \sum_j A_{ij} c_j M_j + \dots} \cong K \sum_i c_i M_i \left(1 - 2 \sum_j A_{ij} c_j M_j \right) \\ &\cong K \left(\sum_i c_i M_i - 2 \sum_i \sum_j A_{ij} c_i M_i c_j M_j + \dots \right) \\ &= K \left[c M_w - 2A_{2,z} (c M_w)^2 + \dots \right] = Kc M_w (1 - 2A_{2,z} c M_w + \dots) \end{aligned} \quad (1.93)$$

$$\cong K \frac{cM_w}{1 + 2A_{2,z}cM_w + \dots}, \quad (1.94)$$

where A_{ij} is the second virial coefficient between species i and j , discussed in Section 1.7.1. We have already demonstrated [see Eq. (1.90)] that in scattering the weight-average molar mass, M_w , is measured in polydisperse samples at low concentrations. It is a higher moment of the distribution than the number-average molar mass measured by osmotic pressure. Similarly, the z -average second virial coefficient $A_{2,z}$, measured by light scattering,

$$\begin{aligned} A_{2,z} &\equiv \frac{\sum_i \sum_j A_{ij} c_i M_i c_j M_j}{(cM_w)^2} = \frac{\sum_i \sum_j A_{ij} c_i M_i c_j M_j}{(\sum_i c_i M_i)^2} \\ &= \frac{1}{M_w^2} \sum_i \sum_j A_{ij} w_i M_i w_j M_j, \end{aligned} \quad (1.95)$$

is a higher moment than the weight-average second virial coefficient $A_{2,w}$, measured by osmotic pressure [Eq. (1.75)]. Measurement of scattered intensity at different dilute concentrations allows determination of the weight-average molar mass M_w and the z -average second virial coefficient $A_{2,z}$.

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} + 2A_{2,z}c + \dots \quad (1.96)$$

This procedure is analogous to determination of the number-average molar mass M_n and weight-average second virial coefficient $A_{2,w}$ from the measurements of osmotic pressure Π at different concentrations [Eq. (1.76) and Fig. 1.22].

It is important to stress that the above treatment is only valid if the wavelength of light λ is much larger than the size of the molecules. Otherwise the angular dependence of the scattered light $I(\theta)$ contains a contribution from the coherent scattering between different parts of the same molecule (called the form factor). In this case, a more sophisticated method of analysis is used, called a Zimm plot, that allows not only determination of the molar mass, but also the size of the molecules. The angular dependence of light scattering is discussed in Section 2.8. Equation (1.96) is recovered only in the small-angle limit.

1.7.3 Intrinsic viscosity

Each polymer coil in a solution contributes to viscosity. In very dilute solutions, the contribution from different coils is additive and solution viscosity η increases above the solvent viscosity η_s linearly with polymer concentration c . The effective 'virial expansion' for viscosity at low concentration is of the same form as Eq. (1.76) for osmotic pressure and Eq. (1.96) for light scattering:

$$\eta = \eta_s(1 + [\eta]c + k_H[\eta]^2c^2 + \dots). \quad (1.97)$$

The term that is linear in concentration contains the **intrinsic viscosity** $[\eta]$ and the quadratic term includes the **Huggins coefficient** k_H , which plays the role of the second virial coefficient for viscosity. Intrinsic viscosity $[\eta]$ is the initial slope of a plot of relative viscosity η/η_s against concentration. Since relative viscosity is dimensionless, the intrinsic viscosity has units of reciprocal concentration. It is proportional to the reciprocal concentration of monomers in a chain's pervaded volume V [Eq. (1.21)]:

$$[\eta] \approx \frac{1}{c^*} \sim \frac{V}{M} \approx \frac{R^3}{M}. \quad (1.98)$$

Intrinsic viscosity is related to the linear size of the coil R and the molar mass M by the **Fox–Flory equation**:

$$[\eta]M \sim V \sim R^3. \quad (1.99)$$

This equation will be derived in Chapter 8. Dilute solution viscosity measurements are important characterization tools for polymers because the Fox–Flory relation shows that the product $[\eta]M$ is proportional to the pervaded volume of the polymer coil.⁹ Since polymers are fractals, their molar mass and their size are related by a power law ($M \sim R^D$), leading to the **Mark–Houwink equation**:

$$[\eta] = KM^a. \quad (1.100)$$

K and a are tabulated for nearly all linear polymers in various solvents, which means that intrinsic viscosity provides a simple effective measure of molar mass. From Eq. (1.98) it is clear that the Mark–Houwink exponent $a = (3/D) - 1$. Representative values of Mark–Houwink coefficients and Huggins coefficients are shown in Table 1.4.

Table 1.4 Representative Mark-Houwink and Huggins coefficients of linear polymers

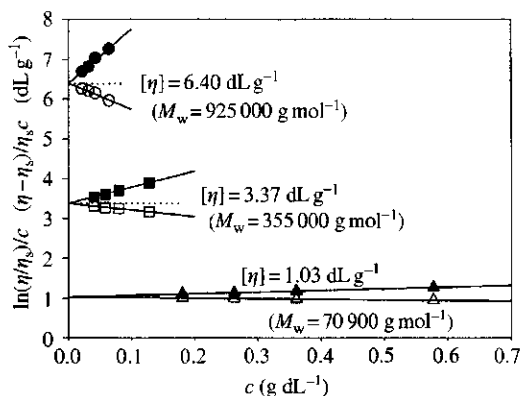
| Polymer | Solvent | $K[(\text{dL g}^{-1})(\text{mol g}^{-1})^a]$ | a | k_H |
|---------------|-------------------------------------|--|-------|---------|
| Polybutadiene | Tetrahydrofuran* at 25 °C | 2.88×10^{-4} | 0.726 | |
| Polybutadiene | Dioxane [†] at 26.5 °C | 1.78×10^{-3} | 0.50 | |
| Polystyrene | Tetrahydrofuran* at 25 °C | 1.10×10^{-4} | 0.725 | 0.35 |
| Polystyrene | Cyclohexane [†] at 34.5 °C | 8.46×10^{-3} | 0.50 | 0.5–0.8 |
| Polyethylene | Xylene at 81 °C | 1.05×10^{-3} | 0.63 | 0.38 |
| Polypropylene | Xylene at 85 °C | 9.6×10^{-4} | 0.63 | |

*Good solvents typically have $0.7 < a < 0.8$ and $0.3 < k_H < 0.4$. [†] θ -solvents have $a = 0.5$ and have k_H increasing with molar mass with $0.5 < k_H < 1.5$.

In practice, dilute solution viscosity is measured at multiple concentrations and two different forms of Eq. (1.97) are used to extrapolate to zero concentration. One form is the **Huggins equation**

$$\frac{\eta - \eta_s}{\eta_s c} = [\eta] + k_H [\eta]^2 c + \dots, \quad (1.101)$$

⁹ The appropriate volume appears to be a combination of static and dynamic coil sizes, as will be discussed in Chapter 8.

**Fig. 1.24**

Determination of the intrinsic viscosity for three different polybutadiene samples in tetrahydrofuran at 25°C. Each sample exhibits linear Huggins (filled symbols) and Kraemer (open symbols) plots that extrapolate to the intrinsic viscosity at zero concentration. All three polymers have Huggins coefficients of 0.37.

where $(\eta - \eta_s)/\eta_s c$ is plotted against mass concentration c . The intercept of the Huggins plot (at $c = 0$) is the intrinsic viscosity and the slope is $k_H[\eta]^2$. Solving for η/η_s and taking the natural logarithm allows the Huggins equation to be rewritten as:

$$\begin{aligned}\ln(\eta/\eta_s) &= \ln(1 + [\eta]c + k_H[\eta]^2 c^2 + \dots) \\ &= [\eta]c + \left(k_H - \frac{1}{2}\right) [\eta]^2 c^2 + \dots\end{aligned}$$

The second result was obtained from expansion of the logarithm $[\ln(1 + x + k_H x^2) = x + (k_H - 1/2)x^2$ for small x]. Dividing this last result by c gives the second extrapolation form, known as the **Kraemer equation**, having the same intercept but a different slope:

$$\frac{\ln(\eta/\eta_s)}{c} = [\eta] + \left(k_H - \frac{1}{2}\right) [\eta]^2 c + \dots \quad (1.102)$$

Figure 1.24 shows experimental determinations of the intrinsic viscosity. When both the Huggins and Kraemer equations provide the same intrinsic viscosity and Huggins coefficient, the higher-order terms in these equations can be safely ignored. On the other hand, if the Huggins and Kraemer plots are curved and do not give the same intercept, viscosity measurements need to be made at lower concentrations.

Owing to the superb precision of viscosity measurements, the intrinsic viscosity can easily be measured to three significant figures, which makes it *by far* the most precise polymer characterization method. However, care must be taken to control the temperature precisely, and polymers with large molar mass ($M \gtrsim 10^6 \text{ g mol}^{-1}$) can shear thin in conventional capillary viscometers.

1.7.4 Size-exclusion chromatography

The entire molar mass distribution, including the higher-order average molar masses, such as M_z , M_{z+1} , etc. can be measured by either **size-exclusion chromatography (SEC)** or ultracentrifuge sedimentation. Owing

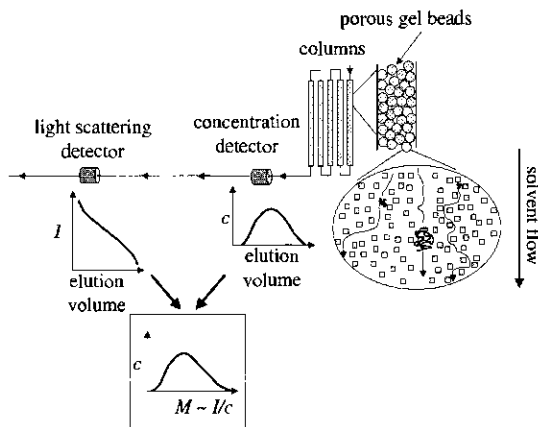


Fig. 1.25
Schematic view of size exclusion chromatography.

to the development of excellent chromatographic columns for SEC, it has completely displaced the ultracentrifuge for characterization of molar mass distribution. Furthermore, modern SEC is highly automated and reasonably precise, making it the most popular method of polymer characterization.

Size exclusion chromatography, also called **gel permeation chromatography** (GPC) continually pumps solvent through a series of columns filled with porous beads (see Fig. 1.25). Often, the beads are polymer gels swollen with solvent. The beads are intentionally made with a variety of pore sizes that span the range of the sizes of macromolecules to be separated. A dilute polymer solution in the same solvent is injected into a small volume of the flowing solvent stream entering the columns. As the polymer solution passes through the columns, the largest polymers are excluded from all but the largest pores, and elute from the columns first. Progressively smaller polymers can explore progressively smaller pores and therefore, larger volumes of the column, and consequently elute later. Thus the separation of molecules in SEC occurs by polymer size rather than by polymer mass.

After separation, the solution passes through a variety of detectors, depending on the information needed for a particular sample. Common detectors include a differential refractometer (for measuring concentration), absorption spectrophotometric detection (such as ultraviolet and infrared), light scattering photometer (for measuring M_w of each eluent), and viscometer (for measuring $[\eta]$ of each eluent). With proper calibration using narrow molar mass distribution standards, SEC can in principle determine the full molar mass distribution, including higher-order averages. However, practical limitations make determination of averages that are higher-order than M_z unreliable. In the best of circumstances with modern SEC equipment and a full complement of detectors, M_z is determined to $\pm 10\%$, whereas M_w can be determined to $\pm 5\%$ from light scattering.

As an analogy describing the SEC process, consider an art museum with an entry on one side and an exit on the other side of the building. On a

sunny Sunday morning the museum opens at 10:00 AM and different groups of tourists enter the museum. Some of them come in big buses on 5 h city tours. These large groups stop at a couple of major paintings and exit the museum less than an hour later. Smaller groups come in vans on special tours of city museums. They visit all the floors of the museum and spend a couple of hours in it. But there are many individual art lovers who visit all of the rooms in the museum and spend a long time in front of many paintings and leave the museum late in the afternoon.

Size exclusion chromatography separates polymers by their size in solution. A given polymer coil can only enter the pores of the column that are larger than the coil. This idea led Benoit to propose a scheme for **universal calibration** of SEC involving the pervaded volume of the coil. The volume within the columns that is accessible to a polymer determines how long the polymer stays in the columns. The amount of solvent that exits the columns between the time the polymer is injected and when it exits the columns is termed the **elution volume**. Benoit's idea is simply that there is a unique relation between the pervaded volume of the coil and its elution volume, for a given set of SEC columns. Hence, both polystyrene and poly(vinyl chloride) with the same pervaded volume will elute from the SEC at the same elution volume. Most modern SEC columns are designed to give a linear relation between the logarithm of pervaded volume [experimentally measured as $[\eta]M$, see Eq. (1.99)] plotted against elution volume over a wide range, as shown in Fig. 1.26. For both very short chains and very long chains, Fig. 1.26 shows departures from the roughly linear calibration curve. When chains are too short, their pervaded volume is smaller than all of the pores in the columns and the SEC no longer separates such short chains because they experience all of the available volume of the columns. This is the downturn in Fig. 1.26 at large elution volume. Similarly, chains that are too long have a pervaded volume that is larger than any of the pores in the column. These long chains pass through the column in the interstitial spaces between beads and hence are also not separated (the upturn at small elution volume in Fig. 1.26).

For strictly linear chains, universal calibration is extremely useful because the Mark–Houwink coefficients have been tabulated for all common linear polymers. The calibration curve allows $[\eta]M$ to be determined from the elution volume. The Mark–Houwink equation [Eq. (1.100)] then allows the SEC measure of $[\eta]M$ to determine the molar mass of the polymer:

$$[\eta]M = KM^{a+1} \Rightarrow M = \left(\frac{[\eta]M}{K} \right)^{1/(a+1)} \quad (1.103)$$

In practice, SEC columns are often calibrated using linear monodisperse polystyrene standards, generating a calibration curve like Fig. 1.26. Then any linear polymer that is soluble in the same solvent, for which a Mark–Houwink equation is known, can have its molar mass determined by this calibrated SEC experiment. The elution volume of the polymer determines $[\eta]M$ from the calibration curve and the Mark–Houwink

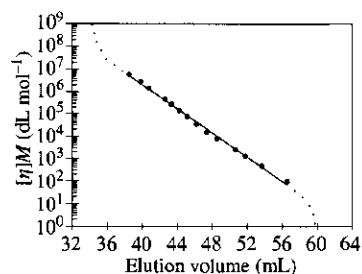


Fig. 1.26

Universal calibration curve for size exclusion chromatography. Data points are polybutadienes in tetrahydrofuran at 25 °C in crosslinked polystyrene columns. There is a reasonably linear region of the calibration curve spanning the data (solid line) but the linear region has its limits (dotted curves).

equation subsequently determines the molar mass from $[\eta]M$. For branched polymers, universal calibration still works. A branched polymer will elute at the same elution volume as a linear polymer with the same pervaded volume. However, unless the Mark–Houwink relation for the branched polymer is known (which is rare) there is no means to convert $[\eta]M$ into a molar mass.

For branched polymers and for linear polymers that do not have an established Mark–Houwink equation, SEC is typically used in conjunction with light scattering and viscosity detectors. These detectors measure the weight-average molar mass and viscosity of each elution volume. In principle, this experiment directly determines both M_w and $[\eta]$ for *any* polymer that is soluble in the SEC solvent, but in practice the M_w determination also requires that the polymer have an appreciable difference in refractive index from the solvent so that in Eq. (1.88), $dn/dc \gtrsim 0.05 \text{ mL g}^{-1}$. Often a new polymerization is not understood sufficiently to know for certain whether the polymer produced will have branched chains present or not, and SEC with multiple detectors is the method of choice for characterizing such polymers. Multiple-detector SEC provides an enormous amount of information in an automated fashion. The weight-average molar mass and intrinsic viscosity of each individual elution volume are determined quite precisely because the concentrations are low enough that second virial and Huggins coefficient terms make negligible contributions.

It is very important to realize that the size separation in SEC is far from perfect. If a perfectly monodisperse sample were instantaneously injected into the columns, the sample would *not* all elute in the same elution volume. This is because the polymer diffuses randomly in the solvent while the solution proceeds through the column. This broadening always makes the polydispersity index measured by SEC larger than the real polydispersity index of the sample, thereby accounting for the discrepancy between theory and experiment at low molar masses in Fig. 1.20.

1.8 Summary

Polymers are formed by repetitive covalent bonding of chemical monomers. The number of monomers in a macromolecule N is its degree of polymerization. Some polymer characteristics, such as degree of polymerization, microstructure, architecture and chemical composition are fixed during polymerization. These characteristics control many important properties of polymeric materials.

A macromolecule can adopt many conformations, defined by relative locations of its monomers in space. Polymer conformations are often self-similar (fractal) with pervaded volume V much larger than their occupied volume Nv_{mon} where v_{mon} is the monomer volume. The overlap volume fraction

$$\phi^* = \frac{Nv_{\text{mon}}}{V}, \quad (1.104)$$

is much less than unity. The overlap parameter P is the average number of chains in a pervaded volume that is randomly placed in the solution. At volume fractions below overlap ($\phi < \phi^*$) the solution is called dilute and the overlap parameter is less than unity ($P < 1$). At volume fractions above overlap ($\phi > \phi^*$) the solution is called semidilute and the overlap parameter $P > 1$.

Synthetic polymers are often polydisperse, containing a mixture of molecules with different molar masses. This mixture is described by a distribution—number fraction (or mole fraction) n_N of molecules with molar mass M_N . The distribution is characterized by its moments, with the k th moment of the number fraction distribution function defined as a sum over the distribution:

$$m_k = \sum_N n_N M_N^k. \quad (1.105)$$

Different molar mass averages are defined as ratios of consecutive moments of the molar mass distribution. The number-average molar mass is the ratio of the first to zeroth moment of the number fraction distribution function (which is equal to the first moment because the normalization of the number fraction distribution makes the zeroth moment unity):

$$M_n \equiv \frac{m_1}{m_0} = \sum_N n_N M_N. \quad (1.106)$$

The weight-average molar mass is the ratio of the second to the first moment of the number fraction distribution function and is equal to the first moment of the weight fraction distribution function:

$$M_w \equiv \frac{m_2}{m_1} = \frac{\sum_N n_N M_N^2}{\sum_N n_N M_N} = \sum_N w_N M_N. \quad (1.107)$$

The polydispersity index is defined as the ratio of the weight- to number-average molar masses M_w/M_n . The polydispersity index is equal to unity for monodisperse polymers (samples with only one molar mass). A larger value of the polydispersity index corresponds to polymeric systems with broader molar mass distributions. Linear condensation polymers typically have $M_w/M_n \cong 2$, while linear addition polymers can have virtually any polydispersity index, depending on the relative rates of polymerization and termination.

Molar masses and molar mass distributions are usually measured in dilute solutions. Osmotic pressure measurements determine M_n and light scattering measurements determine M_w . The entire molar mass distribution can be measured using properly calibrated SEC.

Problems

Section 1.2

1.1 Consider a 'true macromolecule'—a chunk of polybutadiene network of mass 100 g. How many monomers all covalently bonded together does it contain if

the molar mass of a monomer is $M_{\text{mon}} = 54 \text{ g mol}^{-1}$? What is the molar mass of this macromolecule?

Section 1.3

1.2 If two different monomers A and B prefer to react with each other than react with their own kind, explain how you would synthesize the following copolymers:

- (i) alternating copolymer
- (ii) diblock copolymer
- (iii) triblock copolymer

Section 1.4

1.3 Consider a dense globule of polyethylene with molar mass $M = 10^6 \text{ g mol}^{-1}$ in a non-solvent. What is the radius of the globule if the density inside the globule is $\rho = 0.784 \text{ g cm}^{-3}$?

1.4 Consider an ideal polyethylene chain with molar mass $M = 10^6 \text{ g mol}^{-1}$. Its mean-square end-to-end distance is given by

$$\langle R^2 \rangle = Cb^2N,$$

where the monomer length is $b = 2.5 \text{ \AA}$ and the coefficient $C = 5.5$. Estimate its root-mean-square end-to-end distance $\sqrt{\langle R^2 \rangle}$ if the molar mass of the monomer is $M_{\text{mon}} = 28 \text{ g mol}^{-1}$.

1.5 What is the maximum length

$$R_{\text{max}} = bN$$

of a polyethylene chain with molar mass $M = 10^6 \text{ g mol}^{-1}$ and monomer length $b = 2.5 \text{ \AA}$?

1.6 Calculate the fractal dimension of the Koch curve in Fig. 1.27 with the center third of each segment replaced by three sides of a square (instead of two sides of a triangle as discussed in Section 1.4).

1.7 Determine the fractal dimension of a Sierpinski carpet (see Fig. 1.28), constructed by dividing solid squares into 3×3 arrays and removing their centers.

1.8 Calculate the fractal dimension of a Menger sponge (see Fig. 1.29), a three-dimensional version of the Sierpinski carpet. A solid cube is divided into $3 \times 3 \times 3$ cubes and the body-center cube along with the six face-center cubes are removed. The same procedure is repeated for each of the remaining 20 cubes, etc.

1.9 A polymer in a melt is in its ideal state, which is a fractal with fractal dimension $\mathcal{D} = 2$. Consider two such chains, a longer one with degree of polymerization $N_1 = 1000$ and a shorter one with degree of polymerization $N_2 = 250$. What is the ratio of their sizes R_1/R_2 ?

1.10 A linear polymer in a good solvent is a fractal with fractal dimension $\mathcal{D} \cong 1.7$. What fraction of a chain has size (average distance between its two end monomers) equal to half of the average distance between two ends of the whole chain?

1.11 An ideal randomly branched polymer is a fractal object with fractal dimension $\mathcal{D} = 4$. In Chapter 6, we will learn how this polymer can fit into three-dimensional space. What is the ratio of molar masses M_1/M_2 of two ideal randomly branched polymers if the ratio of their sizes is $R_1/R_2 = 3$?

1.12 In Chapter 3, we will learn that a linear polymer confined to an air-water interface is a fractal object with fractal dimension $\mathcal{D} = 4/3$. What is the ratio

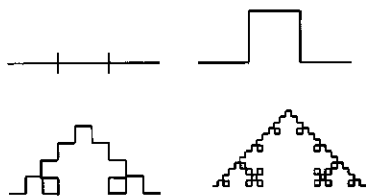


Fig. 1.27
A Koch curve based on squares.

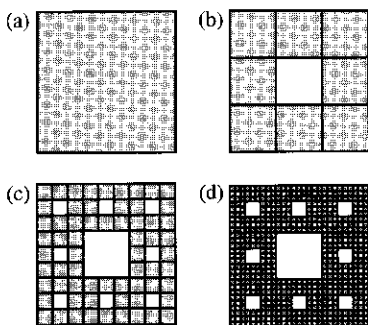


Fig. 1.28
Sierpinski carpet construction: Start with a square (a), divide it into nine equal squares and remove the center one (b). With each of the remaining eight squares, repeat the process (c) and so on (d).

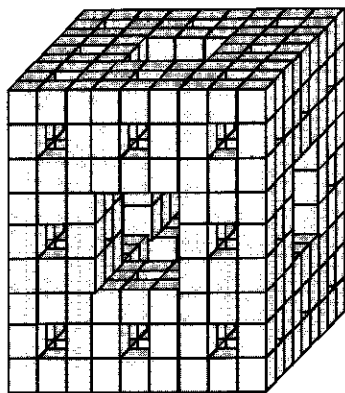


Fig. 1.29
Menger sponge.

of sizes R_1/R_2 of two linear polymers at the air–water interface if the ratio of their molar masses is $M_1/M_2 = 16$?

- 1.13 Give additional examples of: (i) regular fractals; (ii) fractals in nature.

Section 1.5

- 1.14 The density of a 1,4-polybutadiene melt at 298 K is $\rho = 0.895 \text{ g cm}^{-3}$. What is the monomer volume v_{mon} , if the mass of the monomer is $M_{\text{mon}} = 54 \text{ g mol}^{-1}$?
- 1.15 Consider a polystyrene solution with concentration $c = 1 \text{ g L}^{-1}$ in a solvent with density $\rho = 0.9 \text{ g cm}^{-3}$. Estimate the volume of a polystyrene monomer in this solution if the density of bulk polystyrene is $\rho = 1 \text{ g cm}^{-3}$ and the mass of the monomer is $M_{\text{mon}} = 104 \text{ g mol}^{-1}$. What is the volume fraction of polystyrene in this solution?
- 1.16 What is the volume fraction of 1 mg mL^{-1} poly(vinyl chloride) in solution if the volume of each monomer is $v_{\text{mon}} = 75 \text{ \AA}^3$ and the molar mass of each monomer is $M_{\text{mon}} = 62 \text{ g mol}^{-1}$?
- 1.17 Calculate the overlap volume fraction ϕ^* of a polymer with degree of polymerization $N = 10^4$ and monomer volume $v_{\text{mon}} = 100 \text{ \AA}^3$, if its pervaded volume is a sphere with radius 200 \AA .
- 1.18 Consider a solution of rod polymers with degree of polymerization $N = 100$ and end-to-end distance $L = Nb$ with monomer length $b = 5.5 \text{ \AA}$ and monomer mass $M_{\text{mon}} = 75 \text{ g mol}^{-1}$.

(i) What is the pervaded volume of this polymer?

(ii) Is a solution with concentration $10^{-3} \text{ g cm}^{-3}$ dilute or semidilute?

- 1.19 Consider a polymer solution with degree of polymerization $N = 500$, volume fraction $\phi = 10^{-2}$, monomer volume $v_{\text{mon}} = 90 \text{ \AA}^3$ and pervaded volume 10^4 nm^3 . What is the overlap parameter P of this solution?
- 1.20 Consider a 10 mL solution obtained by mixing 20 mg of dry polymer with solvent. The bulk density of the dry polymer is $\rho = 0.8 \text{ g cm}^{-3}$. What is the volume fraction of polymer in this solution? Assume no change of volume upon mixing.
- 1.21 A polymer with molar mass $M = 10^5 \text{ g mol}^{-1}$ is at overlap in a solution with concentration $c^* = 1.67 \times 10^{-2} \text{ g cm}^{-3}$. What is the pervaded volume V of each polymer chain?
- 1.22 Estimate the overlap parameter P for polymers with fractal dimension D in the melt ($\phi = 1$) if the degree of polymerization is N . Estimate the overlap parameter for an ideal chain (with $D = 2$) in a melt with $N = 10^4$ monomer segments.

Section 1.6

- 1.23 Consider five textbooks from the polymer bookshelf; by P. J. Flory consisting of 672 pages, by P. G. de Gennes consisting of 324 pages, by M. Doi and S. F. Edwards consisting of 391 pages, by A. Yu. Grosberg and A. R. Khokhlov consisting of 350 pages and by J. des Cloizeaux and G. Jannink consisting of 896 pages.

(i) What is the number-average number of pages per textbook?

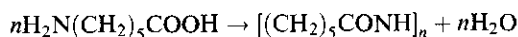
(ii) What is the weight-average number of pages per textbook?

(iii) What is the polydispersity index?

- 1.24 Science Fiction: Three Planets.

(i) On the planet Demos, all major decisions are made by votes of all inhabitants. All votes are counted with equal weight. What kind of average decision is achieved on the planet Demos?

- (ii) On the planet Fatos all major decisions are also made by votes of all inhabitants. Votes on Fatos are counted proportional to the weight of the corresponding inhabitant. What kind of average decision is achieved by this weighted voting on the planet Fatos?
- (iii) On the planet Thinos all major decisions are also made by votes of all inhabitants. Votes on Thinos are counted inversely proportional to the weight of the corresponding inhabitant. What kind of average decision is achieved by this weighted voting on the planet Thinos?
- 1.25** Consider a system consisting of one elephant with mass $M_1 = 10^4$ kg and nine mosquitoes riding on its back with mass $M_2 = 0.1$ g each.
- Calculate the number-average molar mass M_n of this system.
 - Calculate the weight-average molar mass M_w of this system.
 - Calculate the polydispersity index of this system.
 - Which average is appropriate for calculating the damage to your Land Rover in a collision with this system?
- 1.26** Consider the following distribution of polymer chains:
- 10 chains with degree of polymerization 100
 100 chains with degree of polymerization 1000
 10 chains with degree of polymerization 10000
- Calculate the number-average degree of polymerization N_n of this distribution.
 - What is the weight-average degree of polymerization N_w of this distribution?
 - What is the polydispersity index of this distribution?
- 1.27** Consider a blend obtained by mixing 1 g of a polymer with molar mass $M_A = 1 \times 10^5$ g mol⁻¹ and 2 g of the same type of polymer with molar mass $M_B = 2 \times 10^5$ g mol⁻¹.
- Calculate the number-average molar mass M_n of this blend.
 - What is the weight-average molar mass M_w of this blend?
 - What is the polydispersity index of this polymer blend?
- 1.28** A protein sample consists of 80% by weight material with $M = 5 \times 10^4$ g mol⁻¹ and 20% by weight of dimer with molar mass 10^5 g mol⁻¹. Calculate M_n , M_w , and polydispersity index.
- 1.29**
- Is it possible for a number fraction n_N of a chain of N monomers to be larger than the weight fraction w_N of this species? What can you state about the molar mass M_N of this species?
 - Is it possible for a number fraction n_N of a chain of N monomers in a polydisperse sample to be equal to its weight fraction w_N ? What can you state about the molar mass M_N of this species?
- 1.30** The number fraction (or mole fraction) of a protein with molar mass $M_A = 10^5$ g mol⁻¹ in an unknown mixture of different protein species is $n_A = 0.1$. The weight fraction of this protein in the same mixture is $w_A = 0.2$.
- What is the number-average molar mass M_n of the mixture?
 - What is the weight-average molar mass M_w of this mixture?
- 1.31** Show that the k -moment of the number fraction distribution n_N is related to the $(k - 1)$ -moment of the weight fraction distribution w_N [derive Eq. (1.54)].
- 1.32** Consider the condensation polymerization of aminocaproic acid to make nylon 6:



- What is the number-average molar mass M_n at the extent of reaction $p = 0.99$?

(ii) What is the weight-average molar mass M_w and polydispersity index at the same extent of reaction $p = 0.99$?

1.33 At what extent of reaction p is the polydispersity index of a linear condensation polymerization sample equal to $M_w/M_n = 1.5$?

1.34* Prove that the weight-average molar mass is never smaller than the number-average molar mass and therefore the polydispersity index is never less than unity:

$$\frac{M_w}{M_n} \geq 1.$$

1.35 Calculate the degree of polymerization $N_{\max}(p)$ corresponding to the maximum of the most-probable weight fraction $w_N(p)$ [Eq. (1.53)] at the extent of reaction p . Is this value $N_{\max}(p)$ better approximated for small $(1-p)$ by the number-average N_n or by the weight-average N_w degree of polymerization? *Hint:* Expand the logarithm for small $(1-p)$.

1.36* Consider condensation polymerization of f -arm stars. Each star molecule contains one multifunctional monomer B_f and $N-1$ bifunctional monomers AB with condensation reaction possible only between unreacted A and B groups. Arms of the star are polydisperse with each of f arms containing between 0 and $N-1$ monomers AB.

(i) Demonstrate that the number fraction distribution function of N -mers is

$$n_N(p) = \frac{(N+f-2)!}{(f-1)!(N-1)!} p^{N-1} (1-p)^f,$$

where N is the total degree of polymerization of all arms of the star.

(ii) Show that the number-average degree of polymerization is

$$N_n = \frac{(f-1)p + 1}{1-p}.$$

(iii) Calculate the weight-average degree of polymerization and show that as extent of reaction $p \rightarrow 1$, the polydispersity index decreases with the number of arms as

$$\frac{N_w}{N_n} \cong 1 + \frac{1}{f}.$$

1.37* Addition polymerization

(i) Calculate the weight-fraction distribution function w_N for addition polymerization without termination from the Poisson number fraction distribution function n_N [Eq. (1.67)] using

$$w_N = \frac{N n_N}{\sum_{N=1}^{\infty} N n_N}.$$

(ii) Prove that the number-average degree of polymerization of the Poisson distribution is N_n .

(iii) Calculate the weight-average degree of polymerization N_w and polydispersity index for addition polymerization without termination. Does N_w/N_n increase or decrease as the reaction proceeds?

(iv) The number-average degree of polymerization of an addition polymerization sample is $N_n = 100$. What is the polydispersity index of this sample?

* Throughout this book, problems marked with an asterisk are more challenging than those that are not.

Introduction

- 1.38 Prove that the Shultz distribution w_N [Eq. (1.70)] has a maximum at $N = N_n$ for any value of $s > 0$.
- 1.39 List the necessary conditions for formation of a narrow molar mass distribution in addition polymerization.

Section 1.7

- 1.40 The osmotic pressure of a polymer solution at temperature $T = 23^\circ\text{C}$ was measured at several concentrations and is reported in the table below.

| | | | | | |
|--------------------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| c (g cm^{-3}) | 2×10^{-3} | 4×10^{-3} | 6×10^{-3} | 8×10^{-3} | 10^{-2} |
| Π (dyn cm^{-2}) | 508 | 1.04×10^3 | 1.58×10^3 | 2.15×10^3 | 2.74×10^3 |

Determine the number-average molar mass M_n of the polymer and the second virial coefficient of the solution A_2 .

- 1.41 Light scattering measurements at scattering angle $\theta = 3^\circ$ were performed on a dilute polymer solution using a laser with a wavelength $\lambda = 5500 \text{ \AA}$. The refractive index of the solvent is $n_0 = 1.4$ and the refractive index increment of the solution is $dn/dc = 0.1 \text{ cm}^3 \text{ g}^{-1}$. The following data for the Rayleigh ratio were obtained:

| | | | | | |
|---------------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| c (g cm^{-3}) | 5×10^{-4} | 10^{-3} | 1.5×10^{-3} | 2×10^{-3} | 2.5×10^{-3} |
| R_θ (cm^{-1}) | 4.9×10^{-4} | 8.4×10^{-4} | 1.1×10^{-3} | 1.3×10^{-3} | 1.5×10^{-3} |

- (i) What is the value of the optical constant K if one can assume that in dilute solutions $n \cong n_0$?
- (ii) Plot Kc/R_θ as a function of the concentration c and determine the weight-average molar mass M_w and the second virial coefficient A_2 .
- 1.42* Modern light scattering uses a polarized laser, but since much of the older literature used unpolarized light sources, it is useful to understand them. Unpolarized light can be represented as a combination of a vertically and horizontally polarized waves—the first one with electric field oscillating along the vertical x axis and the second one—along the horizontal y axis. The intensities of these two parts of the incident light are $I_x = I_y = I_i/2$. The intensity per unit scattering volume of the vertically polarized scattered wave is $\bar{I}_{\text{polar}}/2$.

- (i) Show that the intensity at scattering angle θ , per unit scattering volume of the horizontally polarized scattered wave, is $(\bar{I}_{\text{polar}}/2) \cos^2 \theta$.
- (ii) Show that the intensity of the scattered light per unit scattering volume using an unpolarized light source valid for any radial position of the detector with scattering angle θ is

$$\bar{I}_{\text{unpolar}} = \frac{2\pi^2 n^2}{\lambda^4 r^2} (1 + \cos^2 \theta) \left(\frac{dn}{dc} \right)^2 \frac{cM}{N_{\text{Av}}} I_i. \quad (1.108)$$

- (iii) Demonstrate that the Rayleigh ratio from an unpolarized light source [Eq. (1.87)] is equal to

$$\begin{aligned} R_\theta^{\text{unpolar}} &\equiv \frac{\bar{I}_{\text{unpolar}} r^2}{I_i} = \frac{2\pi^2 n^2}{\lambda^4} \left(\frac{dn}{dc} \right)^2 \frac{cM}{N_{\text{Av}}} (1 + \cos^2 \theta) \\ &= KcM \frac{1 + \cos^2 \theta}{2}, \end{aligned} \quad (1.109)$$

where K is the optical ratio defined in Eq. (1.89).

- 1.43 The intensity of the incident beam decreases due to scattering following Beer's Law:

$$I_i(z) = I_0 \exp[-\tau(z - z_0)], \quad (1.110)$$

where τ is the turbidity of the sample and $z - z_0$ is the length of the path of the incident beam between the entry into the sample z_0 (with intensity I_0 at z_0) and the point with coordinate z . Turbidity can be obtained from the Rayleigh ratio by integrating the radiated energy over all scattering directions. Using the Rayleigh ratio for an unpolarized light source [Eq. (1.109)], show that the turbidity is

$$\tau = \frac{8\pi}{3} KcM. \quad (1.111)$$

- 1.44 Size exclusion chromatography

A fraction of a polystyrene sample elutes in tetrahydrofuran at 25°C at 48 mL. Estimate the molar mass of this fraction using the universal calibration for this set of columns presented in Fig. 1.26 and the Mark-Houwink coefficients listed in Table 1.4.

- 1.45 Determine the moment of the molar mass distribution measured by intrinsic viscosity of a polydisperse sample.

Bibliography

- Billmeyer, F. W. Jr. *Textbook of Polymer Science*, 2nd edition (Wiley, New York, 1971).
- Chu, B. *Laser Light Scattering: Basic Principles and Practice* (Academic Press, New York, 1991).
- Flory, P. J. *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, New York, 1953).
- Grosberg, A. Yu. and Khokhlov, A. R. *Giant Molecules: Here, There, and Everywhere* (Academic Press, New York, 1997).
- Guinier, A. *X-ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies* (W. H. Freeman, New York, 1963).
- Higgins, J. S. and Benoit, H. C. *Polymers and Neutron Scattering* (Clarendon Press, Oxford, 1994).
- Mandelbrot, B. B. *The Fractal Geometry of Nature* (W. H. Freeman, New York, 1982).
- Morawetz, H. *Macromolecules in Solution*, 2nd edition (Wiley, New York, 1975).
- Morawetz, H. *Polymers: The Origins and Growth of a Science* (Wiley, New York, 1985).
- Painter, P. C. and Coleman, M. M. *Fundamentals of Polymer Science*, 2nd edition (Technomic, Lancaster, 1997).
- Peebles, L. H. *Molecular Weight Distributions in Polymers* (Wiley, New York, 1971).
- Sperling, L. H. *Introduction of Physical Polymer Science*, 3rd edition (Wiley, New York, 2001).

This page is intentionally left blank